ALBERTA OIL SANDS ENVIRONMENTAL RESEARCH PROGRAM

The Evaluation of Wastewaters from an Oil Sand Extraction Plant

HY 3.1

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ALBERTA OIL SANDS ENVIRONMENTAL RESEARCH PROGRAM

RESEARCH REPORTS

These research reports describe the results of investigations funded under the Alberta Oil Sands Environmental Research Program, which was established by agreement between the Governments of Alberta and Canada in February 1975. AOSERP is a 10-year Program designed to direct and coordinate research projects into the environmental effects of the development of the Athabasca oil sands in Alberta

Enquiries pertaining to the Alberta-Canada Agreement or requests for copies of the research reports should be directed to:

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The Evaluation of Wastewaters from an
Oil Sand Extraction Plant

Sub-project HY 3.1

AOSERP Report 5

LETTER OF TRANSMITTAL

The Hon. D. J. Russell
Minister of the Environment
222 Legislative Building
Edmonton, Alberta

and

The Hon. R. LeBlanc
Minister of Fisheries and Environment
Parliament Buildings
Ottawa, Ontario.

Sirs:

Enclosed herein is the report on "The Evaluation of Wastewaters from an Oil Sand Extraction Plant".

This report was prepared for the Hydrology Technical Research Committee of the Alberta Oil Sands Environmental Research Program, under the Alberta-Canada Agreement of 28 February 1975.

Respectfully,

W. Sołodzuk, P.Eng.
Chairman, Steering Committee, AOSERP
Deputy Minister, Alberta Environment

J. S. Tener, Ph.D.
Member, Steering Committee, AOSERP
Assistant Deputy Minister
Environmental Management Service
Environment Canada.

THE EVALUATION OF WASTEWATERS FROM AN OIL SAND EXTRACTION PLANT

DESCRIPTIVE SUMMARY

ABSTRACT

The organic constituents of wastewaters from the existing Athabasca oil sands extraction plant were characterized and quantified. Twenty-one chemical parameters were determined on a total of ten samples taken during November and December, 1975 from the tailings pond dike filter drainage system, the upgrading plant final effluent to the Athabasca River and the intake pond waters. In addition, a number of specific aromatic hydrocarbons and organic sulphur compounds were identified and heavy metals and vanadium were determined.

Tailings pond dike filter drainage samples contained 100-120 mg/l of total organic carbon, 69% of which was extractable with organic solvents. Ninety-two percent of the extractable carbon was in the form of oxygenated compounds, including organic acids (79%), phenols (4.5%), ketones (2.7%), aldehydes (1.9%), organic acid esters (1.5%), amides (1.0%), and quinones (0.2%). Organic sulphur compounds averaged 5.3%, organic nitrogen compounds 1.1% and hydrocarbons 0.04% of the extractable material.

Upgrading plant effluents contained an average of 36 mg/l of total organic carbon, only 15 mg/l of which was extractable. Oxygenated compounds accounted for 30% of the extractable organic carbon, organic sulphur compounds 17%, nitrogen compounds 7% and hydrocarbons 7%. The remaining 6 mg/l of organic carbon was not accounted for.

On the basis of these findings and previously measured water flow data, a calculated daily average of 198 kg (435 lbs) of organic carbon was released to the river from the tailings pond dike filter system and 1460 kg (3,245 lbs) was discharged from the upgrading plant effluent. These amounts corresponded to about 0.8% of the natural organic load of the river.

It is recommended that further studies be conducted on these and other wastewaters on a year-round basis to determine (a) the seasonal variations in amounts of organic constituents, (b) the identity of individual compounds, (c) the toxicity of compound groups and, (d) the physical state of existence

of the organic compounds. It is also recommended that studies be extended to include the characterization of organic constituents in the Athabasca River in order that any environmental effects may be better understood.

BACKGROUND AND PERSPECTIVE

The research conducted for the Hydrology Technical Research Committee of the Alberta Oil Sands Environmental Research Program was based upon a short preliminary study by the same contractor (" Characterization of Wastewaters from the Great Canadian Oil Sands Bitumen Extraction and Upgrading Plant" EPS 5NW-WP-75-6) done under the supervision of the Federal Environmental Protection Services. These studies are the first published on the analytical methods necessary to quantify the organic chemical nature of two types of discharge to the Athabasca River from an existing oil sands extraction plant.

The work provides information on the types of organic chemical compounds that enter the aquatic environment from an existing oil sands extraction plant, and, as such, will be useful to the Hydrology Technical Research Committee in developing the capability to predict the direct physical and chemical impacts in the aquatic environment of oil sands development and useful to other Technical Research Committees in predicting the biological impacts of development.

ASSESSMENT

It is the impression of the Hydrology Technical Research Committee that this work is of a completely satisfactory technical quality. The report has been reviewed extensively by members of the Hydrology Technical Research Committee and the Oil Sands Environmental Study Group. The researchers have incorporated all suggestions in a satisfactory manner.

Study results appear to have several practical applications. The Hydrology Technical Research Committee has subsequently supported the application of this type of research to samples of Athabasca River water and sediments from above and below the oil sands extraction plant, of process effluent water and of coke storage runoff drainage, in order to predict the environmental impacts of organic chemical compounds. In addition, lethal and sub-lethal aquatic faunal studies could utilize the result of

this study.

The Hydrology Technical Research Committee of the Alberta Oil Sands Environmental Research Program accepts " The Evaluation of Wastewaters from an Oil Sand Extraction Plant " as an important and valid research document, recommends it for publication and thanks the researchers for their scientific contributions.

R K Deeprose

R. K. Deeprose, Chairman

Hydrology Technical
Research Committee

THE EVALUATION OF WASTEWATERS FROM AN OIL SAND EXTRACTION PLANT

by

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for

HYDROLOGY TECHNICAL RESEARCH COMMITTEE

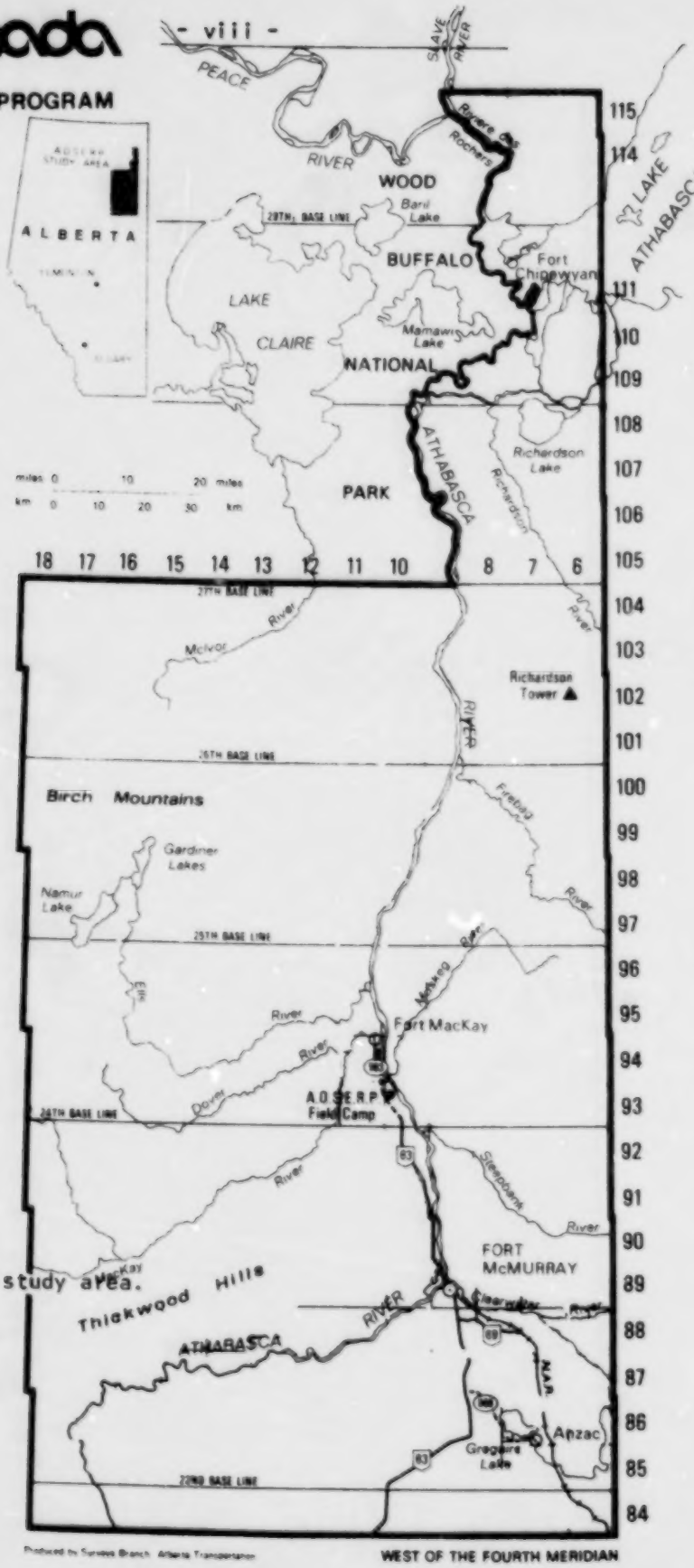
ALBERTA OIL SANDS ENVIRONMENTAL RESEARCH PROGRAM

PROJECT HY 3.1

September 1976

alberta canada

ALBERTA OIL SANDS ENVIRONMENTAL RESEARCH PROGRAM
STUDY AREA



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LIST OF ABBREVIATIONS AND SYMBOLS

AA	atomic absorption	lb(s)	pound(s)
amu	atomic mass units	m	metre
ASTM	American Society for Testing and Materials	m^3	cubic metre
Be	berylium	MeI	methyl iodide
BF_3	boron trifluoride	MeOH	methanol
Co	cobalt	m	milligram (10^{-3} gram)
^oC	degrees Celsius (centigrade)	min	minutes
eV	electron volt	ml	millilitre (10^{-3} litre)
Fe	iron	mm	millimetre (10^{-3} metre)
ft	foot	Mn	manganese
g	gram	N	nitrogen
gal	gallon	NaOH	sodium hydroxide
GC	gas chromatograph	Ni	nickel
GC-MS	gas chromatograph-mass spectrometer	O	oxygen
HCl	hydrochloric acid	Pb	lead
kg	kilogram	pH	hydrogen-ion exponent
KOH	potassium hydroxide	psi	pounds per square inch
ℓ	litre	S	sulfur
		µA	micro ampere
		Zn	zinc

ABSTRACT

The organic constituents of wastewaters from the existing Athabasca oil sand extraction plant were characterized and quantified. Twenty-one chemical parameters were determined on a total of ten samples taken during November and December of 1975 from the tailings pond dike filter drainage system, the upgrading plant final effluent to the Athabasca River and the intake pond waters. In addition, a number of specific aromatic hydrocarbons and organic sulfur compounds were identified and heavy metals and vanadium were determined.

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On the basis of these findings and previously measured water flow data, a calculated daily average of 198 kg (435 lbs) of organic carbon was released to the river from the tailings pond dike filter system and 1460 kg (3,245 lbs) was discharged from the upgrading plant effluent. These amounts corresponded to about 0.8% of the natural organic load of the river.

It is recommended that further studies by conducted on these and other wastewaters on a year-round basis to determine (a) the seasonal variations in amounts of organic constituents, (b) the identity of individual compounds, (c) the toxicity of

compound groups and, (d) the physical state of existence of the organic compounds. It is also recommended that studies be extended to include the characterization of organic constituents in the Athabasca River in order that any environmental effects may be better understood.

THE EVALUATION OF WASTEWATERS FROM AN OILSAND EXTRACTION PLANT

1. INTRODUCTION

One of the prime concerns resulting from recent industrial growth has been the effect of large scale industrial development upon the environment. In response to this concern the government has imposed restrictions and standards for some types of industrial wastes, often requiring industry to find and adopt solutions within a limited time period. In the case of some emissions, such as sulfur dioxide to the atmosphere, the problem is obvious and the necessary technology for control is now available; in other cases the problem is not easily recognized or is not initially perceived as a problem only to later become a major concern. In order to prevent future environmental problems it is necessary to understand what types of wastes may result from a particular industrial process, in what quantities these wastes occur and the effects of their various constituents upon the physical and biological components of the environment. The first step in assessing the environmental impact of industrial effluents and in developing effective control methods is an understanding of the composition of these wastes. Chemical characterization of effluents may provide an understanding of the environmental effects to be anticipated and aid in the development of efficient methods for the control of environmentally toxic materials.

Water quality warrants special attention. In past years water quality was thought of only in terms of inorganic constituents but with increasing demand for industrial growth the role of organic compounds has also emerged as a major concern. This is especially true in the case of petroleum based industries where wastes are almost entirely organic materials. The problem is compounded by the fact that comparatively little is known of the organic constituents or their environmental effects.

Ever increasing demands for energy, together with the decline of conventional crude oil reserves, has led to renewed interest in development of the Athabasca oil sands on a massive scale. The oil sands are a unique deposit requiring recovery

methods entirely different from those of conventional oil deposits. Only the Colorado oil shales comprise an oil deposit of comparable magnitude with the accompanying potential for environmental impact. Although a multitude of companies have spent large amounts of money in research on alternate methods of oil recovery, only one process, the hot water recovery method, is presently feasible. Large scale development with this type of recovery in the foreseeable future will likely require the use and disposal or recycling of large quantities of water. The present bitumen extraction methods are 92-93% efficient and part of the unrecovered oil is being discharged with the water. Present technology has dealt with this problem by retaining the majority of these wastewaters in ponds; eventually this water, with its accompanying organic matter, must return to the environment.

There are several ways to counter the water quality problems arising from large scale oil sand processing. One way involves development of a plant which is a completely closed system - a plant designed and operated in such a manner that no extraction or upgrading plant effluent is discharged to the river, no leaks or runoff of contaminated surface waters occur, and no contact takes place between industrial water and groundwaters. A second alternative is to ensure that any wastewaters in contact with or discharged to the environment are free of all contaminants. A third alternative is to discharge wastewaters from which all toxic compounds have been removed and which contain only innocuous substances. The second and third procedures may be accomplished by developing more efficient means for the recovery of bitumen from the extraction process and by developing more effective means of removing inorganic and organic materials from the wastewater. Knowledge of the chemical composition of organic material in effluents would benefit the development of the above methods.

Investigations have been carried out on shale oil deposits and their process waters in order to establish the identity of indigenous organic compounds. Carboxylic acids were found by

Haug et al. (1967) in the Green River shale oil and process waters from the extraction of this oil contained 1-2 g/ℓ of the organic acids and 50 mg/ℓ of phenols (Cook, 1971). In contrast, phenols were found to be the predominant component of wastewater in the extraction of Estonian Kukersite oil shale (Sharonova, 1968). The simplicity of constituents found in these process waters is directly related to the lighter nature of the oils found in these shales and methods for their removal were uncomplicated. The bitumen recovered from the Athabasca area is much heavier and its constituents are more diverse. For this reason, process waters from Athabasca extraction plants are anticipated to be more complex in terms of their organic constituents.

The current study was initiated jointly by AOSERP through the Environmental Protection Service (Hrudey, 1975) and the Environmental Sciences Centre. Its purpose was to evaluate the constituents of wastewaters from the existing oil sands extraction plant. A comprehensive study evolved to determine the gross classification of organic constituents in a total of ten wastewater samples. The samples were taken from the tailings pond dike filter drainage and from the upgrading plant discharge to the Athabasca River. Twenty-one chemical parameters were examined. The terms of reference for this study are contained in the Appendix (Section 8).

In the five-month period of the study, a basic understanding of the types of compounds present in two types of wastewaters was obtained and the major groups of compounds were classified and quantified. More specifically, investigations revealed organic carbon levels of 100-120 mg/ℓ in tailings pond dike filter drainage samples, approximately 55% of this carbon was in the form of organic acids. In addition, organic sulfur compounds and phenols were found in abundances of 4 and 3 mg/ℓ respectively. Upgrading plant effluents contained concentrations of 30-44 mg/ℓ of organic carbon with no dominant constituents, however the organic acids, sulfur compounds, and phenols were the most abundant compounds detected.

These findings are an important step in evaluating the effects of oil sands processing effluents upon aquatic flora and fauna and in developing methods for the clarification of wastewaters.

2. ANALYTICAL METHODS

2.1 SAMPLE DESCRIPTION AND HANDLING

The study was initiated on September 25, 1975 by way of a contract with AOSERP through the Environmental Protection Service. Delays in obtaining permission to collect samples resulted in a delay of the proposed work schedule by one month. Sampling began on November 3, 1975, when four samples were collected from two different types of wastewater effluents at the Great Canadian Oil Sands site. The first two samples were obtained from the final effluent of the upgrading plant immediately after filtration through straw and before its disposal to the river. The other two samples were taken from one of 72 dike filter drains which emit to the river extraction plant wastewater used in the construction of the tailings pond dike. This water percolates through layers of coke and sand and possibly approximates any groundwater movement from the tailings ponds to the river (Syncrude Environment, 1975). These two sites were resampled on two additional occasions: November 27th and December 18th. In addition, two samples of the intake pond water were obtained: on November 27th a sample was collected close to the tailings pond dike area and on December 18th another was collected next to the intake pipe from the river. Thus, a total of ten samples were taken for chemical characterization of their constituents. All samples are listed in Table 1 according to sampling dates, locations, and sample designation.

Each sample contained sixty litres of water for extraction of the various hydrocarbon compounds to be investigated and an additional thirty litres for individual tests that did not require extraction procedures. These samples were collected in acid cleaned glass containers to avoid contamination by organic compounds. Two

separate one-litre samples were also collected and preserved on site for specific tests; one was treated with nitric acid for vanadium analysis and the other was treated with phosphoric acid and copper sulfate for subsequent phenol determination.

TABLE 1. Sample Description

Sample Designate	Sample Location	Sampling Date
OS-1	Upgrading plant wastewater	Nov. 3/75
OS-2	Upgrading plant wastewater	Nov. 3/75
OS-3	Tailings pond dike filter drainage	Nov. 3/75
OS-4	Tailings pond dike filter drainage	Nov. 3/75
OS-5	Upgrading plant wastewater	Nov. 27/75
OS-6	Tailings pond dike filter drainage	Nov. 27/75
OS-7	Intake pond (close to tailing pond)	Nov. 27/75
OS-8	Upgrading plant wastewater	Dec. 18/75
OS-9	Tailings pond dike filter drainage	Dec. 18/75
OS-10	Intake pond (near pipe outlet of river intake)	Dec. 18/75

Initially, the sixty-litre samples were extracted with benzene at near neutral pH. It was found, however, that this extract contained relatively low amounts of organic material and that further extraction at a lower pH was required to increase the extraction efficiency. The sixty-litre samples were then acidified to pH 2 with hydrochloric acid (HCl) and the remaining organic material was extracted with benzene. The lower pH greatly enhanced the extraction efficiency. Examination of these two extracts individually revealed no chemical differences when compared to a single extract of the same sample at pH 2; remaining samples were then extracted just at pH 2.

Because of the size of the samples to be extracted, a gross extraction procedure was employed whereby multiple extractions with benzene were performed in the large sampling vessels. Mixing was accomplished by using a magnetic stirrer which created a vortex of the benzene in water. The solvent-water contact created by the vortex was sufficient to extract the majority of the extractable organic material with four extractions.

2.2 SEPARATION OF ORGANIC CONSTITUENTS

The complex nature of the investigation was first revealed during preliminary analyses designed to determine how samples and sample extracts could best be proportioned to facilitate the entire range of analyses required. Upon completion of these preliminary investigations a separation scheme was devised to efficiently utilize time and efforts. The resulting procedures along with the various analyses performed on waters and extracts are presented in the accompanying flow diagram.

Two types of analyses were conducted; one type was carried out on water samples as received and the other type was conducted on the benzene extracts of the water samples. A total of eleven different types of chemical analyses were carried out directly on the thirty-litre water samples. Total organic carbon was determined by a commercial carbon analyzer. Amines, nitriles, amides, aldehydes, ketones, phenols, quinones and alcchols were investigated by various spectrophotometric and spectrofluorometric methods while the heavy metals and vanadium were analyzed by atomic absorption techniques.

The extracts of the sixty-litre water samples were divided into five portions, each to be analyzed for different groups of organic compounds. Gross hydrocarbon content, organic nitrogen compounds, organic sulfur compounds and organic phosphorous compounds were each determined directly on one portion of the gross extracts by a variety of gas chromatographic techniques. In addition, infra-red analyses conducted on these gross extracts aided in the identification of major constituents.

Another portion of the total extracts was used for analysis of esters. This required saponification with potassium hydroxide (KOH) to convert esters to free organic acids. Gas chromatography analysis, before and after the saponification procedure, was utilized to quantify the ester component.

A third portion of the total extract was used for the determination of organo-metallic compounds. This was accomplished by concentration of a larger portion of the total extract and examination by X-ray fluorescence methods.

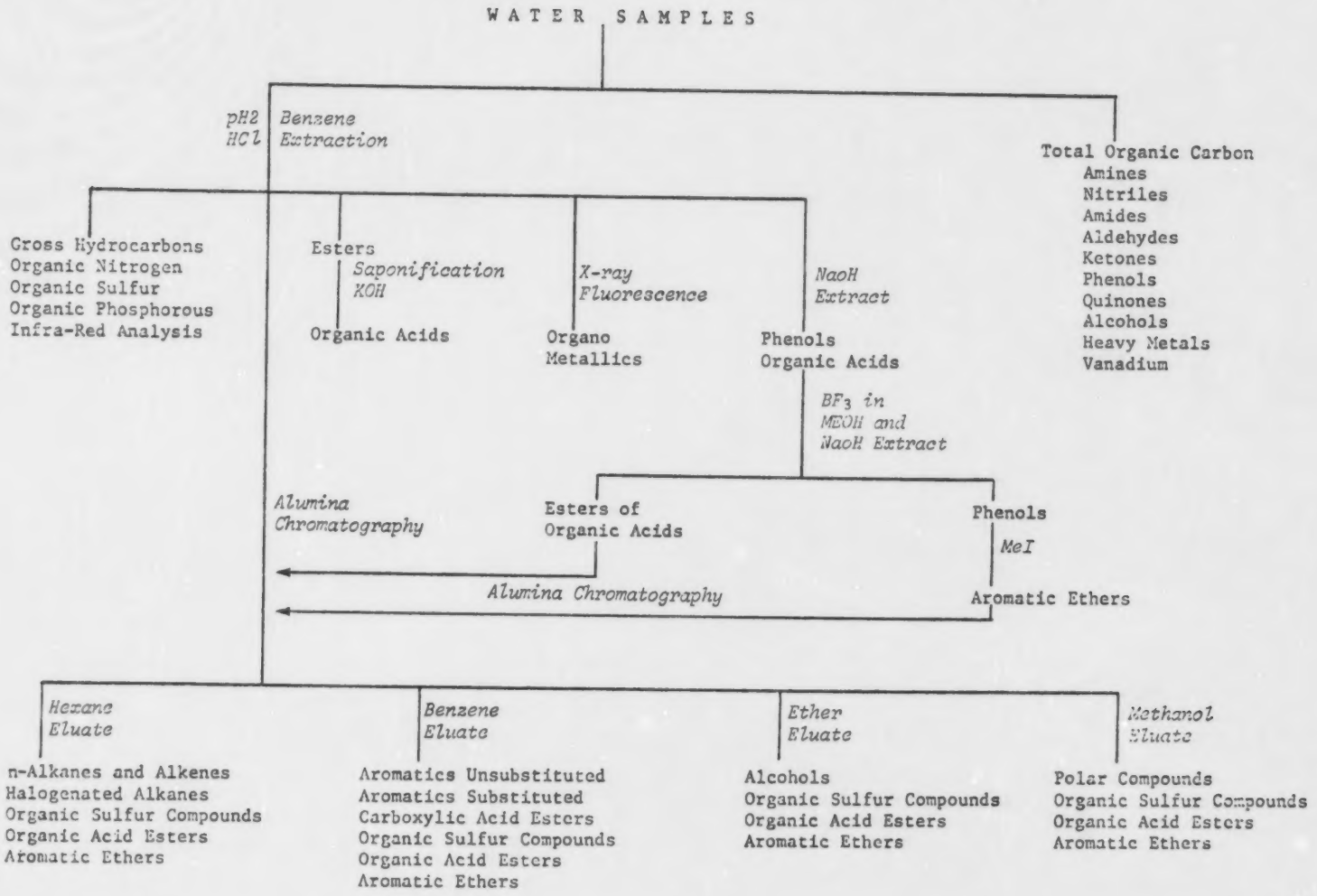

DIAGRAM 1. Flow diagram of the various analytical investigations performed on the wastewaters and extracts of the wastewaters from the oil sand extraction plant.

A large number of organic constituents required an additional separation to allow their detection. This was accomplished by liquid column chromatography on alumina of a fourth portion of the extracts, with elution by four different solvents to affect separation of the various components for further analysis (Strosher and Hodgson, 1975). Alkanes and alkenes, halogenated alkanes and organic sulfur compounds were eluted with hexane. The benzene eluate contained substituted and unsubstituted aromatics, carboxylic acid esters and organic sulfur compounds. Alcohols and some large organic sulfur compounds were eluted with diethyl ether; the polar compounds, including the more polar organic sulfur compounds, were eluted with methanol. After separation, analysis of each group of compounds was obtained by a variety of gas chromatographic methods with further identification of some fractions by mass spectrometry.

The fifth portion of the benzene extract was used for the analysis of phenols and organic acids. Aqueous sodium hydroxide (NaOH) was used to extract the phenols and acids from the remaining hydrocarbons. A subsequent derivatization with boron trifluoride (BF_3) in methanol (MeOH) converted acids to esters and allowed for separation of phenols from acids. Phenols were then converted to aromatic ethers by heating with methyl iodide (MeI). The resulting esters of organic acids and the aromatic ethers derived from phenols were individually chromatographed on alumina columns as was previously described in order to further separate the multitude of compounds within each group. The four fractions separated from each group of compounds were then analyzed by gas chromatography and further investigated by mass spectrometry.

2.3 SPECIFIC ANALYTICAL METHODS

2.3.1 Total Organic Carbon

Analyses for total organic carbon content were carried out on all water samples both as received and after extraction of the soluble organic compounds with benzene.

A Beckman Model 915 total carbon analyzer was used to obtain the organic carbon analysis directly on each water sample.

The principle of detection is the conversion of carbon compounds to carbon dioxide, which in turn is measured by infra-red spectrophotometry. Limits of detection are 2 mg/ℓ with a precision of 5%. Samples were then extracted with benzene and after evaporation by a rotary vacuum apparatus to remove traces of solvent, the water was analyzed again for the organic carbon content. This allowed measurement of the amount of extractable carbon and provided a basis for a mass balance of organic material upon completion of the investigation.

2.3.2 Asphaltenes

The organic matter extracted with benzene from each of the wastewaters was separated into two fractions on the basis of solubility in normal pentane. By definition, the insoluble portion of any crude oil is known as asphaltenes. The precipitated asphaltenes were removed by filtration through a sintered glass disc, after which they were washed with pentane, dried, and weighed.

2.3.3 Aliphatic Hydrocarbons - Alkane and Alkenes

Aliquots of each benzene extract were chromatographed on neutral Brockman activity I alumina to separate groups of compounds for further analysis (Peake, et al., 1972a, 1972b). The first group of compounds eluted from the alumina with n-hexane was the aliphatic hydrocarbons which were subsequently analyzed by gas chromatography (GC). A Varian Aerograph Model 2100 gas chromatograph equipped with dual flame ionization detectors was operated under the following conditions: Glass columns were 3.6 m long and 2 mm inside diameter, packed with 3% SE 30 Ultraphase coated on 60-80 mesh high performance Chromosorb W and, oven temperature programmed from 60° to 265°C at a rate of 10°C per minute. Injection port and detector temperatures were 260°C; helium carrier gas flow rates were 50 ml/min; hydrogen rates were 30 ml/min and air flow was adjusted to give maximum detector sensitivity.

2.3.4 Aromatic Hydrocarbons

The second group of organic compounds to be separated on the alumina column was the aromatic hydrocarbons which were eluted from the column with benzene. Analyses were conducted by gas chromatography as described above and also by combined gas chromatography-mass spectrometry (GC-MS). A Finnigan Model 1015 gas chromatograph-mass spectrometer was used in the identification of specific polycyclic aromatic hydrocarbons. The GC-MS was comprised of a Model 1700 Varian gas chromatograph and a quadrapole mass spectrometer. The GC column was 15 m by 0.064 mm stainless steel SCOT column coated with SE 30 Ultraphase. Conditions were as follows: helium carrier gas flow rate was 5 ml/min; injection port temperature was 250°C and column oven temperature was programmed from 80° to 250°C at 4°C/min. Mass spectrometer conditions were: electron energy at 70 eV and total current at 450 uA.

2.3.5 Polar Organic Compounds

Organic compounds eluted from the alumina column with methanol were designated as O, N, and S polar compounds. It should be noted however that O, N, and S compounds may also appear in hexane and benzene eluates from liquid chromatography on alumina, and that strongly polar compounds may be irretrievably adsorbed by the alumina. In order to further fractionate the polar compounds, two solvents were successively passed through the alumina liquid chromatography column. The first was diethyl ether; the second was the more polar methanol. Gas chromatography, as previously described in 2.3.3, was used to analyze the polar compounds.

2.3.6 Organic Sulfur Compounds

Samples were analyzed for organic sulfur compounds by a gas chromatograph equipped with a flame photometric detector (Martin and Hodgson, 1973) and by combined gas chromatography-mass spectrometry. A Tracor Model 550 gas chromatograph equipped with a flame photometric detector was used to analyze the organic sulfur compounds. The chromatographic column used was a 1.8 m by 2 mm inside diameter

glass column packed with 3% SE 30 Ultraphase coated on 60-80 mesh Chromosorb W. The oven temperature was programmed from 80° to 280°C at 10°C/min, the injection port temperature was 210°C, and the detector temperature was 210°C. The flow rate of helium carrier gas was 80 ml/min, hydrogen flow rate was 180 ml/min, oxygen was 20 ml/min, and air at 100 ml/min. The GC-MS system and operating conditions were as previously described.

The analyses were carried out on the initial benzene extracts as well as the eluates from the alumina liquid chromatography. In this manner it was possible to measure and quantify the total range of sulfur compounds in the effluents as well as examine the various types of compounds separated by liquid chromatography.

2.3.7 Organic Phosphorous Compounds

Examination of effluents for the possible occurrences of organic phosphorous compounds was carried out in much the same manner as were investigations of the organic sulfur compounds. Gross extracts were analyzed by the gas chromatographic technique, utilizing the flame photometric detector with a phosphorous filter.

2.3.8 Halogenated Alkanes and Alkenes

Halogenated hydrocarbons were investigated on a Microtech Model 220 gas-chromatograph fitted with a Ni 63 source in an electron capture detector. A 1.8 m by 6 mm inside diameter glass column was used, packed with 3% OV 17 on Chromosorb W. An isothermal column temperature of 200°C was used with an injector temperature of 230°C, and a detector temperature of 355°C. The carrier gas pressure was 50 psi. In order to reduce the numerous interferences that are encountered by the highly sensitive electron capture detector, samples were fractionated by liquid column chromatography on alumina. Halogenated hydrocarbons were eluted with hexane to try to eliminate the interfering polar compounds containing sulfur, phosphorous, and oxygen.

2.3.9 Carboxylic Acid Esters

Another group of compounds which was found in the extracted organic matter is the dicarboxylic acid esters (plasticizers). This group of compounds was semi-isolated from the majority of the other hydrocarbons by the alumina chromatography technique. They appeared in the benzene eluate, along with the aromatic hydrocarbons and some organic sulfur compounds, and were detected by combined GC-MS methods (Strosher and Hodgson, 1975).

2.3.10 Organic Nitrogen Compounds

A Hewlett Packard Model 7620 gas chromatograph equipped with an alkali flame detector was used to examine the water extracts for nitrogen containing organic compounds. The chromatograph was fitted with a 3.6 m by 6 mm inside diameter glass column packed with 3% OV 101 on Chromosorb W. Oven temperature was programmed from 50° to 270°C at 10°C/min. Injector temperature was 220°C and detector temperature was 350°C. Gas flow of helium was 50 ml/min, of air was 180 ml/min, and the hydrogen flow was adjusted to give maximum detector response.

2.3.11 Heterocyclic Compounds

Heterocyclic compounds contain one or more oxygen, nitrogen or sulfur atoms commonly within a ring structure. No specific test for heterocyclic compounds exists; however, during the course of the previous analysis for sulfur compounds, several heterocyclic sulfur compounds were identified by combined gas chromatography-mass spectrometry methods, as previously described in 2.3.4 and 2.3.6.

The foregoing analyses for the nine types of organic compounds were conducted by gas chromatography on organic material extracted from the effluents. A second type of analysis was conducted directly upon the water samples without prior concentration of the organic matter. Specific tests were conducted for amines, nitriles, aldehydes, ketones, phenols and quinones using the following spectrophotometric and spectrofluorometric techniques.

2.3.12 Amines

The first of the spectrometric tests on the original water samples was for amines. Two specific tests were used--an ASTM spectrophotometric test for the aliphatic amines (ASTM D237-68) and a spectrofluorometric test specifically for the aromatic amines (Dombrowski, 1971). The aliphatic amines that were examined by this method were the primary and secondary amines. Abundances were calculated on the basis of the colorimetric response of a secondary amine, dioctadecylamine, as measured with a Varian Techtron Model 635 spectrophotometer.

The aromatic amines were detected by a fluorometric test that relies on the production of an intensely fluorescent derivative by the coupling of 2,6-diaminopyridine to a diazotized aromatic amine. Quantitation was based on the standard aromatic amine, aniline. Results are, therefore, expressed in terms of the aniline response. Fluorescence was measured with a Turner Model 210 spectrofluorometer.

2.3.13 Nitriles (cyanides)

Nitriles were examined by a spectrofluorometric method. In principle, this method involved reacting a complex of palladium, diaminonaphthalene and selenium with the cyanides which in turn released the fluorescent product, diaminonaphthalene selenide (McKinney, et al., 1972). A standard curve was established using varying quantities of cyanide (as potassium cyanide) and measurement of cyanides in the wastewaters was established from the curve.

2.3.14 Aldehydes

A colorimetric test was conducted for aldehydes in which a derivative of 2,4-dinitrophenylhydrazone was formed. The intensity of the resulting yellow-orange color was read with a spectrophotometer. Ketones also form derivatives, but, as they do so only at much higher concentrations they were not a significant interference. Quantitation was based upon the response of the aromatic aldehyde vanillin (Pesez and Bartos, 1974).

2.3.15 Ketones

The specific test used for ketone detection was a fluorometric method which relied upon the quenching effect that ketones have on the fluorescent compound, β-naphthol (Hynie and Vecerek, 1961). Standard curves were obtained by adding various quantities of acetone to β-naphthol and measuring the differences in fluorescent intensities. Ketone concentrations in samples were accordingly measured by comparison with the acetone response.

2.3.16 Quinones

Quinones were examined by a spectrophotometric method that measured their dinitrophenylhydrazone derivatives (Pesez and Bartos, 1974). Possible interferences of similar oxygen-bonded compounds, such as aliphatic acids, ketones, and aldehydes, were investigated and found to be negligible. Quantitation was based on the standard compound, 1,4-benzoquinone.

2.3.17 Amides

Another group of compounds analyzed by spectrophotometric methods was the amides. The principle of detection relied on the conversion of the amides to the corresponding hydroxomate. The hydroxomate was then developed for colorimetric analysis with ferric chloride (Pesez and Bartos, 1974). Results were based on a standard response curve obtained with a standard acetanilide.

2.3.18 Heavy Metals and Vanadium

Heavy metals and vanadium analyses were also conducted on these original samples. The contract required that vanadium be analyzed by atomic absorption (AA) methods and that X-ray fluorescence be used in the determination of heavy metals. It was found, however, that the X-ray fluorescence methods were not sensitive enough to detect the low quantities of heavy metals present in the water samples. In order to quantitate the heavy metals present, samples were analyzed by the more sensitive atomic absorption techniques.

Separate samples of the wastewaters were obtained at each

sampling point and were immediately preserved with nitric acid for the analysis of vanadium by the atomic absorption technique. Because of the insensitivity of the X-ray fluorescence method, however, these preserved samples were also used for analyses of the heavy metals by AA. The atomic absorption investigations included nine heavy metals in addition to vanadium. These were copper, lead, zinc, manganese, iron, cobalt, nickel, berylium, and cadmium. Two different techniques were used to examine these metals. Solvent extraction was used to concentrate samples for the determination of Cu, Pb, Zn, Ni, and vanadium; the direct aspiration method was used to analyze the remainder of the metals Mn, Fe, Be, and cadmium (Analytical Methods Manual, 1974).

The remaining analyses of organic constituents were carried out on the benzene extracts of the water samples. Analyses of the organo-metallic compounds were conducted directly on the indigenous material, the other analyses required alteration of the extracted organic components to achieve separation, detection and identification of compounds. De-esterification and derivatization techniques were utilized to enhance detection and quantitation of individual groups such as the alcohols, esters, phenols, and organic acids.

2.3.19 Organo-Metallic Compounds

As per the terms of the contract organo-metallic compounds were investigated by X-ray fluorescence methods. These methods of detection for metals are quite insensitive and require concentrations averaging about 50 mg/ℓ for each metal in the water samples. Because such high levels were needed for detection, benzene extracts from about 25 litres of each sample were concentrated and examined by scanning the entire range of a molybdenum lamp. This scan basically covered the fluorescence range of the heavier metals. The sensitivity of detection for this range of metals varied from a high of about 10 mg to a low of about 100 mg.

2.3.20 Alcohols

Alcohols were investigated by two different methods. First, a fluorometric method was used whereby alcohols release a fluorescent compound upon reaction with a complex of vanadium oximate (Pesez and Bartos, 1974). The second method was based on a derivatization procedure that converts alcohols to their corresponding acetal derivatives, thus causing a shift in gas chromatography elution times as compared with their respective elution times in the alcoholic form.

2.3.21 Organic esters

Esters were determined by difference in gas chromatographic response before and after saponification of the extractable material from individual samples. Gross quantitation of organic material was first obtained by gas chromatography. The organic material was then saponified with potassium hydroxide to convert the esters of acids into free acids which are not detected by GC. The de-esterified product was re-examined by gas chromatography and the difference in the two chromatograms was attributed to the ester component.

2.3.22 Phenols

Phenols are common pollutants of wastewaters, and, because of their acidic properties and the caustic extraction process utilized by the present oil sands extraction plant, their presence in the wastewaters was anticipated.

Initially the standard water quality test for phenols--the 4-aminoantipyrene colorimetric test--was utilized. This test, as it is sensitive only to simple phenols and some substituted phenolics, produced a very inaccurate measurement of the large number of compounds which are classed as phenols. Accordingly, other methods for the separation and analysis of phenols were developed.

In the first alternative method, determination of phenols was based on differences in acidity values. Sodium bicarbonate extractions were used to remove the more acidic organic acids from

benzene extracts of the original water samples. These sodium bicarbonate extractions were followed by a series of sodium hydroxide extractions, which separated the less acidic phenols from the remaining neutral hydrocarbons. The sodium hydroxide solution, containing phenols, was then acidified and the phenols were extracted, converted to aromatic ethers, and finally analyzed by gas chromatography and by combined gas chromatography-mass spectrometry. Results by this method showed the presence not only of phenols but also of substantial amounts of organic acids, indicating a considerable overlap in the acidity of the two groups of compounds.

A more definitive separation and analytical method was then developed. Phenols and organic acids were extracted from the bulk of the organic material with sodium hydroxide and transferred to a suitable solvent. The organic acids were then separated on the basis of their chemical reactivity. Organic acids are alkylated by reaction with boron trifluoride in methanol but phenols are not; thus, the acidic phenols could be separated from the neutral organic acid esters by sodium hydroxide extraction. A methyl iodide alkylation was then employed to convert phenols to aromatic ethers for analysis by gas chromatography and combined GC-MS.

Fractionation of the phenols, now in the form of aromatic ethers, was accomplished by liquid column chromatography on alumina. The four solvents hexane, benzene, ether and methanol were used once again to determine the extent at which varying polarities of phenolic compounds existed.

2.3.23 Organic Acids

Organic acids were separated, derivatized and measured by gas chromatography as was described in the previous phenol analysis section.

3. RESULTS AND DISCUSSION

A large number of analytical data has been amassed during the course of this investigation. Information on separation techniques, analytical methods, and methods for the identification of organic compounds are presented in the preceding sections. In the following sections, an attempt is made to integrate the data and provide an overview of the results.

3.1 TOTAL ORGANIC CARBON

Organic carbon analyses were initially carried out on both original and extracted water samples in order to provide a measurement of extraction efficiency. The values thus obtained were also required to complete a mass balance of extracted versus recovered organic constituents, and eventually to determine whether the majority of organic compounds were being detected.

TABLE 2. Organic Carbon Content of Waters

Sample No.	Original Carbon	Extractable Carbon	Residual Carbon	Per cent Extractable Carbon
Upgrading Plant Effluents				
OS-1	33	14	19	42
OS-2	32	13	19	41
OS-5	44	17	27	39
OS-8	36	15	21	42
Tailings Pond Dike Filter Drainage				
OS-3	102	70	32	69
OS-4	98	68	30	69
OS-6	113	73	40	65
OS-9	120	89	31	74
Intake Waters				
OS-7	16	4	12	25
OS-10	15	3	12	20

Of the two wastewaters examined, the tailings pond dike drainage samples exhibited the largest concentrations of total organic carbon (98-120 mg/ℓ). The upgrading plant effluents contained relatively low concentrations of total organic carbon (32-44 mg/ℓ).

The water intake samples contained much lower levels, only 15-16 mg/ℓ of total organic carbon (Table 2). The residual organic carbon values were 30-40 mg/ℓ in tailings pond dike effluents, 19-27 mg/ℓ in upgrading plant wastewaters and 12 mg/ℓ in the intake waters. These results show that 65%-74% of the organic carbon was extracted from tailings pond dike wastewater samples, 39%-42% from upgrading plant effluents and, 20%-25% from intake waters. The differences in extraction efficiency may be attributed to several causes, however it is presumed that the major differences are directly related to: (a) the association of organic constituents with particulate matter in upgrading plant wastewaters and intake waters (tailing pond effluents exhibited no appreciable amounts of particulate), and (b) the occurrence of unextractable humic and fulvic acids.

Organic carbon, regardless of its form of existence in these samples, is measured in this study on the basis of organic carbon in the water as sampled. With the aquisition of the total organic carbon content and the amount of extractable organic carbon, the following investigations were carried out to determine what types of organic compounds were contained within the extractable carbon fraction.

3.2 ASPHALTENES

Chemically, asphaltenes are materials with molecular weights in the order of $1\text{-}5 \times 10^3$. Although the most powerful modern techniques have been applied in the investigations of asphaltenes, the structure of these compounds is still largely undefined. They appear to consist of a core of five stacked sheets, each sheet being composed of an average of 16 condensed aromatic rings (Speers and Whitehead, 1969). Contained within, or attached to this core are aliphatic hydrocarbon chains, oxygen, sulfur and nitrogen atoms and trace metals such as nickel and vanadium. The asphaltene content of the upgrading plant effluents ranged from 0.50 to 0.61 mg/ℓ or from 3.0 to 4.1% of the extractable organic carbon. This compares with 17% asphaltenes measured in the crude bitumen.

3.3 ALIPHATIC HYDROCARBONS

Results by GC showed that aliphatic hydrocarbons are most abundant in the upgrading plant wastewater and are almost non-existent in the tailings pond dike filter drainage and intake waters. Concentrations in the upgrading plant wastewaters ranged from 0.52 to 0.78 mg/ℓ, whereas the tailings pond dike effluents were 0.01 mg/ℓ and intake samples were 0.01 mg/ℓ (Table 3).

TABLE 3. Organic Constituents of Water and Other Samples

Sample No.	Alkanes and Alkenes (mg/ℓ)	Aromatics (mg/ℓ)	Polar Compounds (mg/ℓ)
Upgrading Plant Effluent			
OS-1	0.78	0.25	0.20
OS-2	0.74	0.23	0.22
OS-5	0.67	0.37	0.17
OS-8	0.52	0.48	0.26
Tailing Pond Dike Filter Drainage			
OS-3	0.01	0.02	0.20
OS-4	0.01	0.02	0.19
OS-6	0.01	0.02	0.21
OS-9	0.01	0.03	0.33
Intake Waters			
OS-7	0.01	0.005	0.013
OS-10	0.01	0.002	0.046
	(mg/g)	(mg/g)	(mg/g)
Synthetic Crude	183*	210*	10.5
Coke	0.012	0.023	1.09
Crude Bitumen	157	72	28

* Excluding low molecular weight compounds below nC_8

Aliphatic hydrocarbons in the upgrading plant wastewaters consisted mainly of branched and cyclic alkanes. Normal straight chain alkanes in the range nC_8 to nC_{30} were also present, as is indicated by the peaks rising above the "hump" on the gas chromatogram in figure 1. This hump, created by compounds unresolved by

gas chromatography, is evidence of an extremely complex mixture of branched and cyclic saturated compounds, and possibly alkenes. Tailings pond dike drainage and intake waters also contain some normal alkanes (Figures 2 and 3), however, the majority of the aliphatic hydrocarbons were again in the form of branched and cyclic compounds.

For the purpose of comparison, aliphatic hydrocarbons were separated from crude bitumen, synthetic crude oil, and coke produced by the present oil sand extraction and upgrading processes. Examination of the resulting gas chromatograms (Figures 4, 5, and 6) shows that the normal alkanes contained in the upgrading plant wastewaters more closely resemble those of the synthetic crude and coke than those of the crude bitumen. Differences in the chromatograms are largely caused by loss of low boiling compounds. The molecular weight range of the unresolved branched and cyclic compounds in the dike drainage is intermediate to those of the synthetic crude and the coke, as is shown by the retention time of the hump maxima. The gas chromatograms clearly indicate that the aliphatic hydrocarbons in the upgrading plant wastewaters are primarily generated during the oil sands processing rather than being natural constituents of the insitu bitumen.

The tailings pond dike drainage waters contain relatively small amounts of aliphatic hydrocarbons--a number of which give well resolved chromatographic peaks at retention times coincident to branched and cyclic compounds. These peaks are not apparent in the crude bitumen, synthetic crude oil, or coke, indicating that these hydrocarbons may be generated during the extraction or processing of the bitumen. Alternatively, these hydrocarbons may be present in very small quantities in the raw bitumen and be selectively dissolved in the water during processing.

3.4 AROMATICS

The second group of compounds to be analyzed by gas chromatography were the aromatic hydrocarbons which had been eluted from the alumina column with benzene. Aromatic compounds extracted from the wastewaters ranged in size from two ring substituted naphthalenes to multiringed compounds, and were similar in variety to those found in many crude oils. Quantities as measured by gas chromatography were: 0.23 to 0.48 mg/ℓ in upgrading plant effluents, 0.02 to 0.03 mg/ℓ in tailings pond dike drainage and 0.002 to 0.005 mg/ℓ in intake waters (Table 3).

Additional examination of the upgrading plant wastewaters by combined gas chromatography-mass spectrometry methods (Strosher and Hodgson, 1975) revealed the presence of at least sixteen aromatic compounds in the mass range of 146-246 atomic mass units (amu). A typical mass spectrum of an aromatic compound found in the upgrading plant water effluents is shown in Figure 7. The sixteen compounds which could be tentatively identified are listed in Table 4. Other aromatics were also present, but they either have yet to be identified or have molecular weights greater than 246 amu. Aromatics in this higher molecular weight range are of particular importance, as a number of them display carcinogenic activity (Hartwell and Shubik, 1951).

The tailings pond dike drainage contained lesser amounts of aromatics than the process waters; nevertheless, gas chromatography showed a complex mixture with many individual compounds present (Figure 9). These compounds, although aromatic in nature, have yet to be individually separated and identified. In contrast, the intake pond waters showed almost no aromatic response (Figure 10).

For comparison purposes, the aromatics fractions were separated from crude bitumen, synthetic crude oil, and coke and analyzed by gas chromatography (Figures 11, 12, and 13). The aromatic responses of these fractions were not in every case identical to the responses detected in the wastewaters, however, the aromatics of the upgrading plant effluent did more closely resemble those of

TABLE 4. Aromatic Hydrocarbons Tentatively Identified in Wastewater Extracts

Molecular Weight	Compound	Molecular Formula
142	Methylnaphthalene	$C_{11}H_{10}$
156	Dimethylnaphthalene	$C_{12}H_{12}$
156	Ethylnaphthalene	$C_{12}H_{12}$
168	Methylbiphenyl	$C_{13}H_{12}$
178	Diphenylacetylene	$C_{14}H_{10}$
182	Diphenylethane	$C_{14}H_{14}$
182	2-Ethylbiphenyl	$C_{14}H_{14}$
190	1,4-Dimethyl-2,5-diisopropylbenzene	$C_{14}H_{12}$
192	Methylanthracene	$C_{15}H_{12}$
202	Pyrene	$C_{16}H_{10}$
204	Cadinene	$C_{15}H_{24}$
206	Dimethylanthracene	$C_{16}H_{14}$
242	Methylchrysene	$C_{19}H_{14}$
242	Methylbenz(a)anthracene	$C_{19}H_{14}$
246	1,2,4,5-tetraisopropylbenzene	$C_{18}H_{30}$

the synthetic crude and the coke rather than those of the bitumen. The upgrading plant effluent contained both lower molecular weight aromatics, as was found in the synthetic crude, and higher molecular weight compounds, as found in the coke. This is in sharp contrast with the crude bitumen which exhibited no major distinct aromatic peaks. Thus, as was the case with the aliphatic hydrocarbons, the aromatic hydrocarbons in the upgrading plant effluent appear to be derived from the oil sands processing rather than being natural components carried over from the raw bitumen. The dike drainage also exhibited an array of aromatic compounds more in keeping with the synthetic crude and coke than the bitumen.

3.5 POLAR ORGANIC COMPOUNDS

The total concentration of polar compounds in each water sample as determined by gas chromatography is given in Table 3. Upgrading plant wastewaters ranged from 0.17 to 0.26 mg/ℓ, dike drainage from 0.19 to 0.33 mg/ℓ, and intake waters from 0.01 to 0.05 mg/ℓ.

A comparison of the amounts and relative composition of aliphatic hydrocarbons, aromatic hydrocarbons, and polar compounds in the upgrading plant and tailings pond effluents clearly demonstrates important fundamental differences. The polar compounds make up 87% of these compounds in the drainage from the tailings pond but they comprise only 17% of the same three groups of compounds in the process water. In the process waters the majority of this organic matter (56%) is in the form of aliphatic hydrocarbons.

Gas chromatograms of the separated polar compounds are presented in Figures 14 to 25. In the case of upgrading plant effluent, both the diethyl ether fraction and the methanol eluate contained many resolved peaks as well as a hump of unresolved material. The majority of the material, an average of 61%, was contained in the more polar methanol fraction. In contrast, 71% of the polar compounds were contained in the diethyl ether fraction of the tailings ponds dike drainage extract, again indicating a fundamental difference in the nature of the pollutants in the two

types of effluent. The crude bitumen contained 27.8 mg/g polar compounds, of which 50% was in the ether fraction; the synthetic crude oil contained 10.5 mg/g, of which 59% was in the ether fraction; and the coke contained 1.09 mg/g, of which only 1% was eluted by diethyl ether.

3.6 ORGANIC SULFUR COMPOUNDS

All samples analyzed by gas chromatography with a flame photometric detector produced organic sulfur responses. These responses varied from 0.1 to 0.4 mg/ℓ in the intake waters, from 2.1 to 2.9 mg/ℓ in the upgrading plant wastewaters, and from 3.0 to 5.4 mg/ℓ in the dike drainage wastewaters (Table 5).

TABLE 5. Organic Sulfur and Phosphorous Compounds in Water Extracts (mg/ℓ)

Sample No.	Sulfur Compounds	Phosphorous Compounds
Upgrading Plant Effluent		
OS-1	2.5	<0.003
OS-2	2.1	<0.003
OS-5	2.9	<0.003
OS-8	2.6	<0.003
Tailings Pond Dike Filter Drainage		
OS-3	3.0	<0.005
OS-4	3.3	<0.005
OS-6	4.2	<0.005
OS-9	5.4	<0.005
Intake Waters		
OS-7	0.4	<0.001
OS-10	0.1	<0.001

Compounds ranged from low molecular weight mercaptans, identified by gas chromatography in the production effluent, to a dimethyl substituted thiobenzofluorene of mass 262 detected by combined gas chromatography-mass spectrometry, also in the production effluent. Nine sulfur compounds ranging in molecular weight from 148 to 262 were tentatively identified in the upgrading plant effluent on the basis of their parent ion and their characteristic

fragmentation patterns (Table 6). A typical spectrum of a peak isolated by gas chromatography-mass spectrometry is shown in Figure 26 and was identified as 2,5-dimethylbenzo(b)thiophene. Many compounds, other than the nine listed in Table 6, were detected but have not, as yet, been identified.

TABLE 6. Organic Sulfur Compounds Tentatively Identified in Wastewater Extracts

Molecular Weight	Compound
148	5-methyl-2,3-benzothiophene
162	2,4-dimethylbenzo(b)thiophene
162	2,7-dimethylbenzo(b)thiophene
162	7-ethylbenzo(b)thiophene
170	1,3-dihydro-4,6-dimethylthieno(3,4-C)thiophene
198	4-methyldibenzothiophene
212	dimethylnaptho(2,3-B)thiophene
220	1,4-di-(1-thiaethyl)naphthalene
262	8,10-dimethyl-11-thiabenzo(b)fluorene

Sulfur specific flame photometric responses obtained by gas chromatography of each fraction--hexane, benzene, diethyl ether, and methanol--from the upgrading plant effluent, dike drainage, and intake waters are shown in Figures 27 to 30, 31 to 34, and 35 respectively. The distribution of sulfur compounds among the four fractions of the tailings pond dike drainage reflects the abundance of polar organic constituents in this effluent. The majority of the sulfur compounds occurred in the ether and the methanol fractions, 39% and 40% of the total respectively. For comparison, the sulfur response obtained during the gas chromatography of crude bitumen is given in Figure 36.

Organic sulfur compounds from the upgrading plant wastewaters were more evenly distributed through the hexane, benzene, ether, and methanol fractions, being 28%, 32%, 11%, and 29%

respectively. This distribution is in keeping with that of the coker gas oil shown in Figure 37.

3.7 ORGANIC PHOSPHOROUS COMPOUNDS

In the analyses of the wastewaters it was found that the occurrences of organic sulfur compounds caused some interferences in the determination of phosphorous; interference levels of the organic sulfur compounds were exceptionally low (0.001 mg/ℓ for each sulfur compound) and no detectable amounts of phosphorous compounds were found above these interference levels (Figure 38). It is therefore concluded that total concentrations of organic phosphorous compounds in all samples were all less than 0.005 mg/ℓ.

3.8 HALOGENATED ALKANES AND ALKENES

The analyses for halogenated compounds detected very low concentrations--about 1.0×10^{-7} mg/ℓ in the tailings pond dike drainage and 15×10^{-7} mg/ℓ in the upgrading plant effluents. Because of interferences in these analyses, the values must be regarded as the maximum concentrations of halogenated compounds in these wastewaters. Massive interferences in the analyses of six of the samples was caused by organic sulfur compounds. These samples did not respond to removal of interfering compounds by column chromatography as in 2.3.8, and the results obtained are not reported.

3.9 CARBOXYLIC ACID ESTERS

Abundances of these plasticizers were relatively low compared with the rest of the organic material in the benzene eluate. However, two of these compounds were detected in upgrading plant wastewaters and dike drainage effluents. They were identified as di-n-butyl phthalate and bis (2-ethyl hexyl) phthalate, and were present in amounts of about 0.001 mg/ℓ each. These compounds are widely used in the plastics industry and are commonly found in industrial and municipal effluents.

3.10 ORGANIC NITROGEN COMPOUNDS

The analysis of nitrogen compounds was conducted upon extracts of the tailings pond dike drainage waters and upgrading plant effluents by gas chromatography. Concentrations of nitrogen compounds detected were low, about 0.01 mg/ℓ in both types of samples. These values were calculated on the basis of the alkali flame detector response to azobenzene. Responses to other nitrogen compounds vary according to the molecular weight of the compound and the number of nitrogen atoms it contains, but it is unlikely that the concentrations of nitrogen compounds of molecular weight lower than 250 exceeded 0.1 mg/ℓ in either effluent.

3.11 HETEROCYCLIC COMPOUNDS

Seven heterocyclic sulfur compounds were identified in upgrading plant wastewaters and are listed in Table 6. These comprise a variety of substituted thiophene structures ranging from a methyl benzothiophene of mass 148 to a dimethylnapthothiophene of mass 212. These represent the majority of the 2.9 mg/ℓ of sulfur compounds detected in the upgrading plant wastewaters. A mass spectrum typical of the substituted thiophenes which were separated from the upgrading plant effluent is shown in Figure 26. Similar compounds were predominant in the tailings ponds dike drainage.

3.12 AMINES

Aliphatic amines, as measured colorimetrically, occurred in concentrations of 0.07 to 0.12 mg/ℓ in upgrading plant effluents, from 0.02 to 0.04 mg/ℓ in tailings pond dike drainage waters, and 0.02 mg/ℓ in intake pond waters (Table 7). Aromatic amines were present in even lower concentrations in the upgrading plant wastewaters, tailings pond dike drainage effluent, and intake pond waters, each of which contained less than 0.001 mg/ℓ.

TABLE 7. Organic Compounds in Waters Detected By Colorimetric Tests (mg/ℓ)

Sample No.	Aliphatic Amines	Aromatic Amines	Nitriles	Aldehydes	Ketones	Quinones	Amides
Upgrading Plant Effluent							
OS-1	0.08	<0.001	0.07	0.86	0.52	0.08	1.00
OS-2	0.07	<0.001	0.06	0.83	0.44	0.09	0.87
OS-5	0.08	<0.001	0.02	0.89	0.44	0.10	0.86
OS-8	0.12	<0.001	0.02	0.88	0.48	0.10	0.85
Tailings Pond Dike Filter Drainage							
OS-3	0.02	<0.001	0.04	1.22	2.04	0.14	0.73
OS-4	0.02	<0.001	0.05	1.38	1.96	0.15	0.77
OS-6	0.03	<0.001	0.06	1.45	2.01	0.16	0.70
OS-9	0.04	<0.001	0.04	1.38	2.04	0.16	0.90
Intake Waters							
OS-7	0.02	<0.001	<0.01	0.51	0.05	0.05	0.61
OS-10	0.02	<0.001	<0.01	0.40	0.09	0.05	0.60

3.13 NITRILES (CYANIDES)

Quantities of cyanides detected in the wastewaters were low. Upgrading plant effluents revealed levels of 0.02 to 0.07 mg/ℓ and tailings pond dike drainage wastewater samples exhibited 0.04 to 0.06 mg/ℓ. Intake waters were both less than 0.01 mg/ℓ (Table 7).

3.14 ALDEHYDES

Aldehydes detected ranged from 1.22 to 1.45 mg/ℓ in tailings pond dike drainage samples, from 0.83 to 0.89 mg/ℓ in upgrading plant wastewaters, and from 0.40 to 0.51 mg/ℓ in intake waters (Table 7).

3.15 KETONES

The analyses for ketones showed the presence of 1.96 to 2.04 mg/ℓ in the tailings pond dike drainage samples whereas the upgrading plant effluents contained 0.44 to 0.52 mg/ℓ (Table 7). Intake waters were considerably lower in ketone concentrations at 0.05 to 0.09 mg/ℓ. These amounts were too low to interfere with the previous aldehyde test.

3.16 QUINONES

Concentrations of the quinones were highest in the tailings pond dike drainage samples where 0.14 to 0.16 mg/ℓ were found. Upgrading plant effluents contained 0.08 to 0.10 mg/ℓ and the intake waters exhibited levels of about 0.05 mg/ℓ (Table 7).

3.17 AMIDES

The following levels of amides were detected: 0.85 to 1.0 mg/ℓ in upgrading plant effluents, 0.70 to 0.90 mg/ℓ in tailings pond dike drainage and 0.61 mg/ℓ in intake pond waters (Table 7).

The preceding seven colorimetric tests showed greater amounts of several types of compounds in the tailings pond dike filter drainage and the upgrading plant waters as compared to the intake pond waters, but showed little significant difference in the two types of effluents. Only in the case of the ketones were substantial differences noted, with four times as much in the dike filter drainage as in the upgrading plant effluent.

The carbonyl group of ketones and aldehydes which increases the acidity of hydrogen attached to the α carbon makes the lower molecular weight compounds soluble in water. The finding of ketones in the tailings pond dike filter drainage water is consistent with the caustic extraction process now used in the oil sands recovery.

3.18 HEAVY METALS AND VANADIUM

The results of the various analyses for heavy metals indicated that vanadium was the most abundant of the metals, occurring in the upgrading plant wastewaters in amounts of 0.25 to 0.60 mg/ℓ (Table 8). Tailings pond dike drainage effluents and intake waters contained considerably lower amounts of vanadium--0.001 to 0.002 and <0.001 mg/ℓ respectively. Thus it appears that the major source of vanadium in effluents from the existing oil sands plant is the upgrading process rather than the extraction process. The next most abundant metal was iron, which was measured at levels of about 0.25 mg/ℓ in tailings pond dike drainage and up to 0.5 mg/ℓ in the upgrading plant and intake waters. Manganese was the third most abundant with levels of about 0.02 mg/ℓ in tailings pond dike drainage effluents, 0.03 in intake waters, and 0.05 mg/ℓ in upgrading plant effluents. The only other metal detected at levels above 0.01 mg/ℓ was nickel, which occurred in the upgrading plant effluents at levels of 0.02 to 0.04 mg/ℓ. The remaining metals were found in abundances very near detectable limits.

3.19 ORGANO-METALLIC COMPOUNDS

Under the terms of the contract, organo-metallic compounds were to be analyzed in the water samples by X-ray fluorescence methods. As was previously discussed under section 2.3.19 of the report, this method is very insensitive. Even in a large sample of 25 litres no amounts of heavy metals were detected in the extractable organic material. Although the sensitivity of the methods varies for individual metals, the amount of organo-metallic compounds present in the effluents was less than a detection limit of about 2 mg/ℓ.

TABLE 8. Heavy Metals and Vanadium (mg/ℓ)

Sample	Copper	Lead	Zinc	Manganese	Iron	Cobalt	Nickel	Berylium	Cadmium	Vanadium
Upgrading Plant Effluent										
OS-1	0.003	<0.004	0.004	0.056	0.45	0.002	0.021	<0.005	0.001	0.25
OS-2	0.003	<0.004	0.001	0.053	0.44	0.003	0.019	<0.005	0.001	0.27
OS-5	0.004	<0.004	0.005	0.041	0.50	<0.002	0.025	<0.005	0.001	0.60
OS-8	0.005	<0.004	0.001	0.031	0.47	<0.002	0.41	<0.005	0.001	0.48
Tailings Pond Dike Filter Drainage										
OS-3	<0.001	<0.004	0.007	0.020	0.25	<0.002	0.003	<0.005	0.001	0.002
OS-4	<0.001	<0.004	0.007	0.018	0.26	<0.002	0.004	<0.005	0.001	0.002
OS-6	<0.001	<0.004	0.006	0.016	0.23	<0.002	0.003	<0.005	0.001	0.001
OS-9	<0.001	<0.004	0.003	0.017	0.18	<0.002	0.003	<0.005	0.001	0.001
Intake Waters										
OS-7	0.002	<0.004	0.001	0.033	0.55	<0.002	0.004	<0.005	0.001	<0.001
OS-10	0.006	<0.004	<0.001	0.027	0.40	<0.002	0.002	<0.005	0.001	<0.001

3.20 ALCOHOLS

Investigations by both the fluorescent complex method and gas chromatography revealed no trace of alcohols (less than 0.001 mg/ℓ) in either the tailings pond dike filter drainage or the upgrading plant effluent.

3.21 ORGANIC ESTERS

Esters of organic acids were present in tailings pond dike drainage samples at levels up to 1.2 mg/ℓ. Upgrading plant wastewaters contained an average of 0.70 mg/ℓ organic acid esters and intake pond waters less than 0.1 mg/ℓ (Table 9). These amounts corresponded with the large amounts of organic acids found and discussed in a later section (3.23).

TABLE 9. Esters, Phenols and Organic Acids in Waters and Water Extracts (mg/ℓ)

Sample No.	Esters	Phenols Colorometric	Phenols by GC	Organic Acids by GC	Organic Acids by weight
Upgrading Plant Effluent					
OS-1	0.79	0.15	0.18	1.21	------
OS-2	0.95	0.15	0.10	1.04	------
OS-5	0.69	0.16	0.10	1.00	------
OS-8	0.85	0.19	0.16	0.91	------
Tailings Pond Dike Filter Drainage					
OS-3	1.22	<0.01	3.77	43.8	55.1
OS-4	1.15	<0.01	3.59	38.5	52.8
OS-6	1.03	<0.01	3.10	38.5	58.3
OS-9	0.95	0.01	2.95	57.5	69.3
Intake Waters					
OS-7	0.09	<0.01	0.08	0.59	------
OS-10	0.01	<0.01	0.06	0.28	------

3.22 PHENOLS

As described in the previous analytical section, 2.3.22, there are several weaknesses in the standard method for the analysis of phenols. It is, however, the accepted standard method, the basis upon which water quality standards are established, and does provide a means of comparison with values obtained in other waters. Abundances of phenols as indicated by this method were 0.19 mg/ℓ in upgrading plant effluents. There was no response to this method from tailings pond dike drainage samples or intake waters. This lack of a response to the colorimetric test for phenols showed only that simple phenols and some substituted phenols were not present. It did not indicate that all types of phenolic compounds were absent, consequently alternative methods of phenol analysis were applied. Phenol abundances in upgrading plant wastewaters obtained by these newly developed analytical methods reached 0.18 mg/ℓ, a very good correlation with the 0.19 mg/ℓ obtained by the standard phenol test. In contrast, however, the tailings pond dike drainage samples were found to contain 3.0 to 3.8 mg/ℓ of phenolic material as compared with less than 0.01 mg/ℓ measured by the standard test (Table 9). Examination by mass spectroscopy of the phenolic material separated by this new procedure (2.3.22) from the tailings pond dike drainage waters confirmed that the material indeed contained phenols and not organic acids. Similar analysis of the intake waters indicated that phenolics were present in levels of about 0.07 mg/ℓ.

Fundamental differences between the phenolics present in the upgrading plant wastewaters and those in the tailings pond dike filter drainage were revealed by chromatography on alumina. The upgrading plant wastewaters revealed the greatest amount of simple phenols in the hexane eluate at 76% (Figure 39), thus indicating that the majority of the phenols in the upgrading plant wastewaters were the simple phenols, and thereby explaining the positive response to the standard test. The remaining three fractions from the alumina column were proportionately lower in phenolic content--3% for the benzene fraction (Figure 40), 11% for the ether fraction (Figure 41),

and 9% for the more polar methanol fraction (Figure 42). In contrast, phenols from tailings pond dike drainage samples exhibited much higher polarity than those from the upgrading plant effluents. Hexane and benzene fractions from the tailings pond dike drainage sample revealed 1% phenolic content each (Figures 43 and 44). The more polar ether fraction contained the greatest amount at 88% (Figure 45), whereas the methanol fraction revealed 10% phenols (Figure 46). The lack of simple phenols in the tailings pond dike drainage, as shown by the absence of phenols in the hexane and benzene fractions, would explain the failure of the standard test to indicate the presence of phenols in these samples.

Thus, the alumina separation technique revealed a major difference between the phenols in the two wastewaters. Simple phenols, as determined by the colorimetric test, were confirmed as being the major contributor to the phenol content of upgrading plant wastewaters. Tailings pond dike drainage samples however, exhibited a more complex variety of phenolic compounds that were not detected by colorimetric tests.

3.23 ORGANIC ACIDS

Abundances of organic acids in the tailings pond dike drainage samples ranged up to 58 mg/ℓ making them by far the most abundant single group of compounds present (Table 9). Upgrading plant wastewaters contained an average of 1.0 mg/ℓ and intake waters a surprisingly high 0.5 mg/ℓ. Because of the large amounts of acids present in dike drainage waters, it was possible to confirm the gas chromatographic analysis by obtaining dry weights of the acid fractions. Dry weights were 10 to 20% greater than values obtained by gas chromatography, indicating that the standard used in the GC analysis was of lower molecular weight than the unknown organic acids.

The organic acid esters were further fractionated by liquid column chromatography on alumina, The hexane eluate of upgrading plant wastewaters contained 18% of the esterified organic acids (Figure 47) while the benzene fraction contained 3% (Figure 48).

The more polar ether and methanol cuts contained 65 and 14% respectively (Figures 49 and 50). The distribution of the esters from upgrading plant wastewaters throughout the four eluants indicates the presence of a wide range of organic acids with differing polarities. In comparison, tailings pond dike drainage waters once again exhibited a lack of simpler compounds in the hexane eluate at 1% (Figure 51). The majority of the organic acid esters in this sample were contained in the benzene and ether eluates at 47 and 48% respectively (Figures 52 and 53). The more polar methanol fraction revealed only 4% of the total esterified acids (Figure 54). This distribution, unlike that displayed for the upgrading plant effluents, indicated the presence of a narrower range of organic acids. The tailings pond dike drainage samples were almost void of the simpler and the more polar structures. The occurrence of these compounds in the benzene and ether fractions indicates the probability of aromatic structuring rather than aliphatic, however, further separation techniques are required to enhance the identification of individual components by mass spectroscopic methods.

4. SUMMARY AND CONCLUSIONS

4.1 UPGRADING PLANT EFFLUENTS

Upgrading plant effluents contained an average of 36 mg/ℓ of organic carbon of which 15 mg/ℓ was extractable organic material. Organic material may exist in wastewaters in several forms; as dissolved organic compounds, as dispersed or micellar material, as suspended carbon particles, and as material adsorbed on the surface of suspended inorganic particles. Dissolved organic compounds and dispersed organic material may be readily extracted from wastewaters with solvents such as benzene; compounds adsorbed on the surface of inorganic particles are not readily extracted and carbon particles are not extractable from the water at all. The fact that over 50% of the organic carbon present in the wastewaters is not extractable indicates either that it occurs as discrete carbon particles or that it is strongly adsorbed on surfaces.

Oxygen-containing compounds, including organic acids, organic acid esters, phenols, aldehydes, ketones, quinones, and amides, are the most abundant group of compounds present in the upgrading plant wastewaters. Such compounds account for 30% of the extractable organic matter and occur at concentrations averaging 4.3 mg/ℓ. These compounds may be indigenous to the original oil sands bitumen, but more likely they are formed during processing of the extracted bitumen.

A second major group of compounds found in the upgrading plant effluents were the heterocyclic sulfur compounds, largely substituted benzothiophenes. These compounds represented 17% of the extractable organic matter, or approximately 2.7% sulfur in the total extract. The presence of such sulfur compounds is in keeping with the relatively high sulfur content of Athabasca bitumen (about 5%) and the conversion of organic sulfur compounds to the stable benzothiophene. Nitrogen-containing compounds, detected primarily as amides, accounted for 7% of the extractable organic carbon in the upgrading plant wastewaters, or 1.0 mg/ℓ in the original water. Most of these compounds likely originated in the oil sands bitumen.

Hydrocarbons themselves made up a surprisingly small percentage of the extractable organic carbon in the upgrading plant wastewaters--only 7% or about 1.0 mg/ℓ in the water. The majority of the hydrocarbons (67%) were aliphatic in nature; the remaining 23% were aromatic. The aliphatic hydrocarbon composition resembled that of the synthetic crude, and was likely contributed from the upgrading process rather than being indigenous to the bitumen. A mass balance of extracted versus recovered organic constituents is contained in Table 10.

4.2 TAILINGS POND DIKE DRAINAGE WATERS

Tailings pond dike drainage waters contained an average of 108 mg/ℓ total organic carbon of which 69% or 75 mg/ℓ was in the form of extractable organic carbon. This relatively high level of extractable carbon indicates that the organic compounds are likely either directly dissolved in the tailings pond dike drainage waters or are dispersed in a micellar form.

TABLE 10. Mass Balance of Organic Constituents of Waters (mg/ℓ)

Sample No.	Extracted Organic Carbon	Recovered Organic Constituents					Percentage of Carbon Accounted for
		Hydrocarbons	Oxygenated Compounds	Nitrogen Compounds	Sulfur Compounds	Others	
Upgrading Plant Effluent							
OS-1	14	0.03	3.64	1.15	2.5	0.73	65
OS-2	13	0.97	3.45	1.00	2.1	0.72	63
OS-5	17	1.04	3.22	0.96	2.9	0.68	52
OS-8	15	1.00	3.38	0.98	2.6	0.87	59
Tailings Pond Dike Filter Drainage							
OS-3	70	0.03	63.5	0.79	3.0	0.20	96
OS-4	68	0.03	61.0	0.84	3.3	0.19	96
OS-6	73	0.03	66.1	0.78	4.2	0.21	98
OS-9	89	0.04	76.8	0.98	5.4	0.33	94
Intake Waters							
OS-7	4	0.02	1.37	0.63	0.4	0.01	61
OS-10	3	0.01	0.89	0.62	0.1	0.05	56

Most of the extractable organic matter consisted of oxygenated compounds (89%) the majority of which were in the form of free organic acids (88%). Thus, by far the most abundant compounds in the tailings pond dike drainage waters were the organic acids which averaged 59 mg/ℓ. These acids are not the aliphatic fatty acids commonly found in living plants, but are likely a vast array of multiring substituted aromatic acids. Organic acids may have been generated from the oil sands bitumen during the upgrading process, but more likely they are preferentially dissolved from the bitumen during the alkali extraction process, and are thereby concentrated in the water. Of the other oxygen-containing compounds, phenols were most abundant with concentrations of 3.4 mg/ℓ. Again these compounds are not simple phenols but are likely multiring phenolic compounds.

Organic sulfur compounds averaged 4.0 mg/ℓ in the tailings pond effluent, or 5% of the extractable organic matter. The types of sulfur compounds in these samples were more complex in nature than the benzothiophene structures from upgrading plant wastewaters, and they likely came directly from the oil sand bitumen during extraction.

Nitrogen compounds were present in very low amounts, averaging 0.85 mg/ℓ or 1.1% of the extractable organic matter. Aliphatic and aromatic hydrocarbons were present in even lower concentrations, about 0.03 mg/ℓ. The fact that neutral hydrocarbons are not readily soluble in water, and the fact that the tailings pond dike drainage had flowed through coke and sand filters which would remove dispersed hydrocarbons accounts for these values.

From the analytical data it is apparent that organic pollutants in the tailings pond dike drainage and in the upgrading plant effluents are different in chemical character. The effects of such organic compounds upon aquatic flora and fauna would depend upon the concentrations of these compounds in the waters of the Athabasca River which would, in turn, depend upon the volumes of wastewaters released. The toxicity to aquatic life of a few

chemical compounds such as phenols and low molecular weight hydrocarbons has been established (Leithe, 1973), but little is known of the effects of complex mixtures of compounds such as the organic acids predominant in the tailings pond dike drainage waters. At present the major flow into the river appears to be of upgrading plant wastewaters rather than of tailings pond dike drainage (Hrudey, 1975). Calculations based upon these wastewater flow data (recorded Aug. 1975) reveal that the upgrading plant effluent flowing at 41,000 cubic metres (9 million imperial gallons) daily releases an average of 1470 kg (3,245 pounds) of organic carbon per day to the river. The tailings pond dike drainage, flowing at 1,800 cubic metres (400,000 imperial gallons) per day releases an average of 198 kg (435 pounds) of organic carbon daily. During the November sampling period the Athabasca River flow was 2.03×10^6 m^3 (4.47×10^9 gal) per day (Water Survey of Canada, Inland Waters Directorate) and, calculated on the basis of a total organic carbon content of 10 mg/ℓ (Water Quality Branch, Inland Waters Directorate) it carried a load of approximately 203,000 kg (448,000 pounds) of organic carbon daily. Thus, the total contribution of these two effluents to the organic carbon content of the river is roughly equal to 0.8% of the natural organic load. Comparisons of the chemical composition of the organic compounds in wastewaters with naturally occurring compounds in the river water cannot be made at this time. Studies of the natural organic constituents in the river have not as yet been initiated. Other possible sources of organic pollutants such as drainage from the coke storage area would also require chemical analysis.

The present study conducted over a short time period has provided an insight into the amounts and types of organic pollutants which may be derived from oil sands processing. The study was very limited in scope. The following recommendations for continuation of the study are accordingly made, in order that a more complete understanding of the potential problems arising from large scale oil sands development may be gained.

5. RECOMMENDATIONS

5.1 The current investigation was initiated in November of 1975 and sampling operations included only the months of November and December so that analytical investigations could be completed by April of 1976, the end of the contract period. This limited time approach allowed for sampling of effluent streams only through a very narrow time frame, and only the production wastewaters effluent and one portion of the tailings pond dike drainage were accessible. Sampling over such a short period of time during the winter months may not be representative of actual year-round conditions.

It is therefore recommended: that the existing study by continued with monthly sampling over a continuous period of at least one year.

5.2 The current study was limited to two types of wastewater samples, one from the upgrading process and one from the tailings pond dike drainage. Other areas of concern lie within so-called effluents or run-offs from coke storage areas, which occur mainly in the warmer months. A more comprehensive sampling approach would achieve an overall view of the entire organic load that might be associated with the water from oil sands plants of similar design.

It is recommended: that similar analyses be conducted upon other water discharges from the plant, including leachate from the coke piles, groundwater from the tailing sand disposed area, and other discharges or seepages at the discretion of AOSERP and EPS.

5.3 In the present study a number of groups of compounds have been analyzed and quantitatively measured and some individual compounds have been identified. Considerably more effort will be required, however, to identify specific compounds which might cause the tailing pond dike drainage to be toxic (Hrudey, 1975). Organic acids are by far the most abundant class of organic compounds, at least in the tailings pond dike drainage system. These will therefore require the greatest effort in the classification of individual compounds. Organic sulfur compounds are the second most abundant

component of these waters and will also require further investigations to establish their exact identities. Phenols, though not one of the major constituents of the wastewaters, are present in levels far above those that impart undesirable taste and odor to potable water (Leithe, 1972). Therefore, the phenols also warrant further investigation.

All three groups are, in fact, likely to contribute to environmental problems within natural aquatic systems, especially in the concentrations in which they occur (Boylan and Tripp, 1971). Other compounds that are less abundant but could pose future problems are the polycyclic aromatic hydrocarbons. This class of organics contains a variety of compounds with varying degrees of carcinogenic activity (Hartwell and Shubik, 1951) and should be further investigated to determine the extent of their existence.

It is recommended: that further characterization of the organic constituents be conducted, including identification of specific compounds--primarily organic acids, organic sulfur compounds, phenols, and aromatic hydrocarbons.

5.4 The identification of potentially toxic organic compounds produced during extraction and processing of oil sands bitumen is an essential step in determining the effects of these compounds on the aquatic environment into which they are released. Gross classification of groups of compounds has been accomplished in the present study and some specific compounds have been identified.

It is recommended: that studies in cooperation with an appropriate bioassay laboratory be initiated to further identify, separate, and measure the toxicity of major groups of organic compounds existing in oil sand wastewater effluents.

5.5 In order to formulate methods for the removal of organic materials from water it is imperative to determine the physical state in which they exist. The organic constituents of the wastewaters may be dissolved, in micellar suspension, or adsorbed on particulate matter. Characterization will require the examination

of both filtered and unfiltered waters for at least the major classes of organic compounds and for total organic carbon content. Once the characterization of species and occurrences is achieved, methods for their removal can be developed. This study can be applied to holding pond waters as well as effluent samples, thus making possible not only clearer effluents but also more efficient recovery of petroleum products.

It is therefore recommended: that further studies be conducted to determine the physical state of the organic compounds (i.e., dissolved, dispersed, or associated with particulate matter).

5.6 In order to complete the overall study of the effects of oil sands processing on water quality in terms of organic content it is essential to extend these investigations to the river system itself. Background levels of the organic content of waters upstream from extraction plants are required so that, with additional sampling from downstream, the extent to which these extraction plants contribute to the organic load can be established. The information obtained from a river study would also be a major asset to additional biological studies of the river in this area.

It is therefore recommended: that river water samples be taken at intervals above and below the existing plant for analysis of organic components and of other biologically important organic compounds and that these studies be coordinated with biological investigations now being carried out on the Athabasca River.

It is anticipated that studies of this magnitude would require at least a three-year time period to complete. In view of the importance of this topic to evaluating the impact of future oil sands development upon water quality in a major river system of northern Alberta it is recommended that such a three year study be undertaken.

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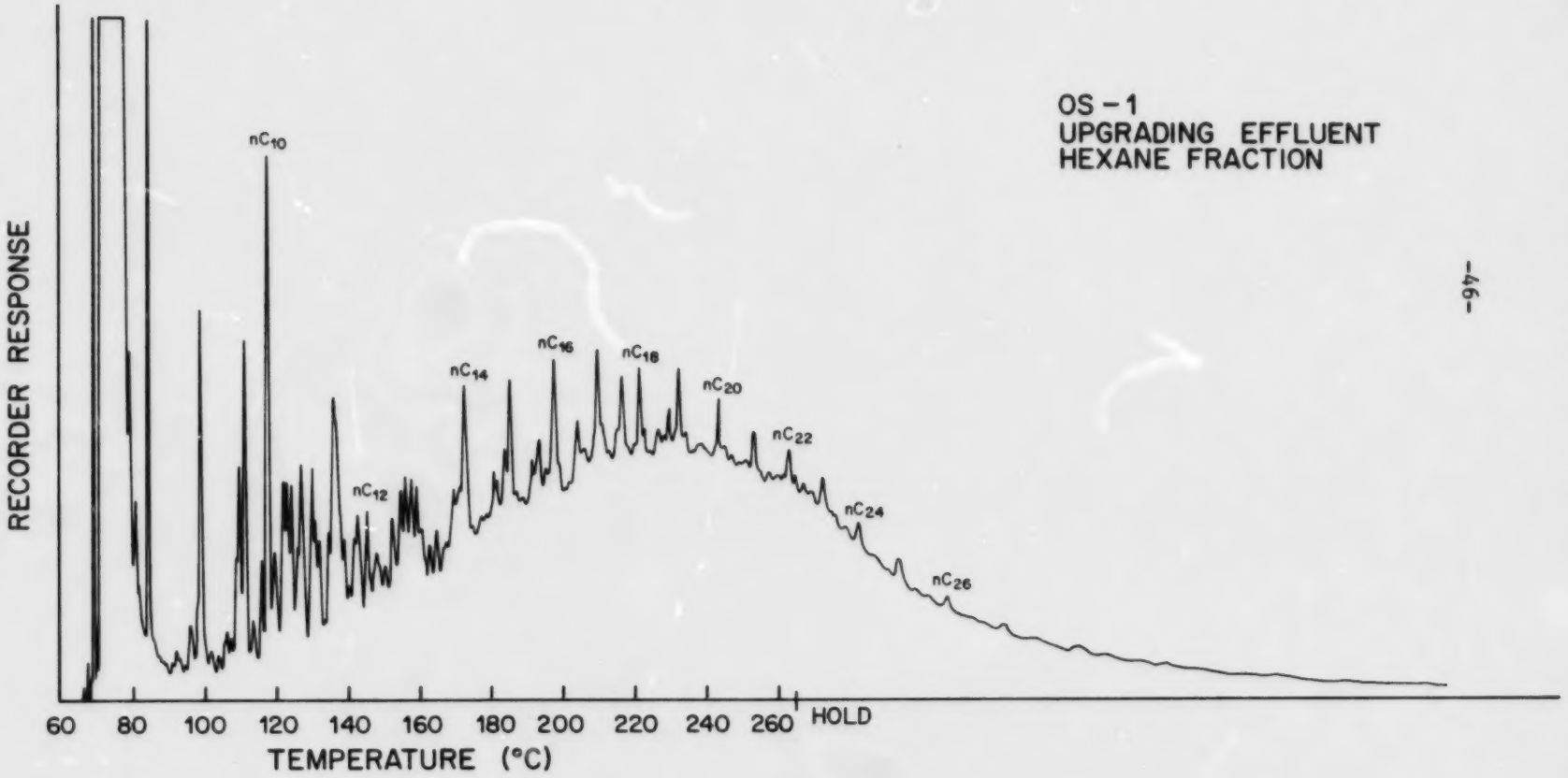
OS – 1
UPGRADING EFFLUENT
HEXANE FRACTION
RECORDER RESPONSE
nC10
nC12
nC14
nC16
nC18
nC20
nC22
nC24
nC26
60 80 100 120 140 160 180 200 220 240 260 HOLD
TEMPERATURE (°C)

Figure 1

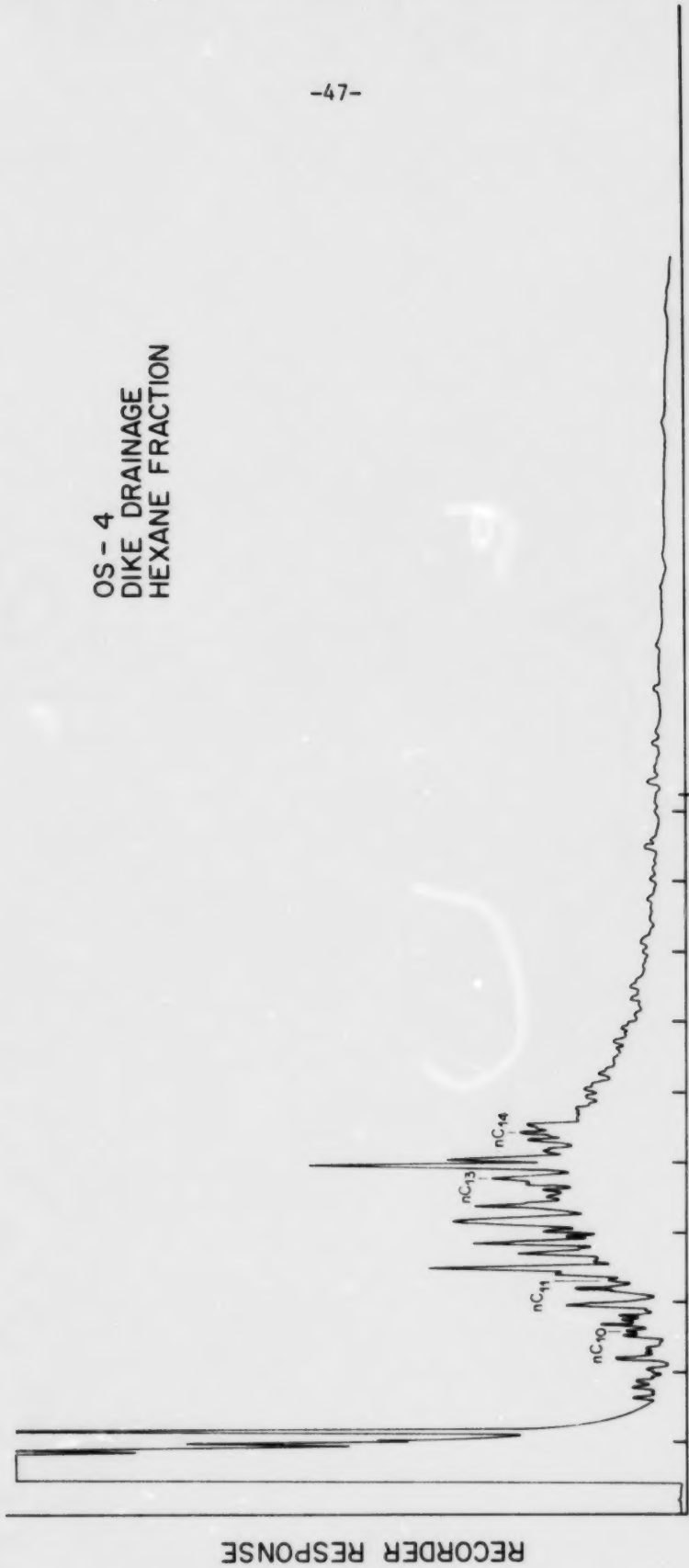
OS - 4
DIKE DRAINAGE
HEXANE FRACTION
RECORDER RESPONSE
60
80
100
120
140
160
180
200
220
240
260
HOLD
TEMPERATURE (°C)
nC10
nC11
nC13
nC14

Figure 2

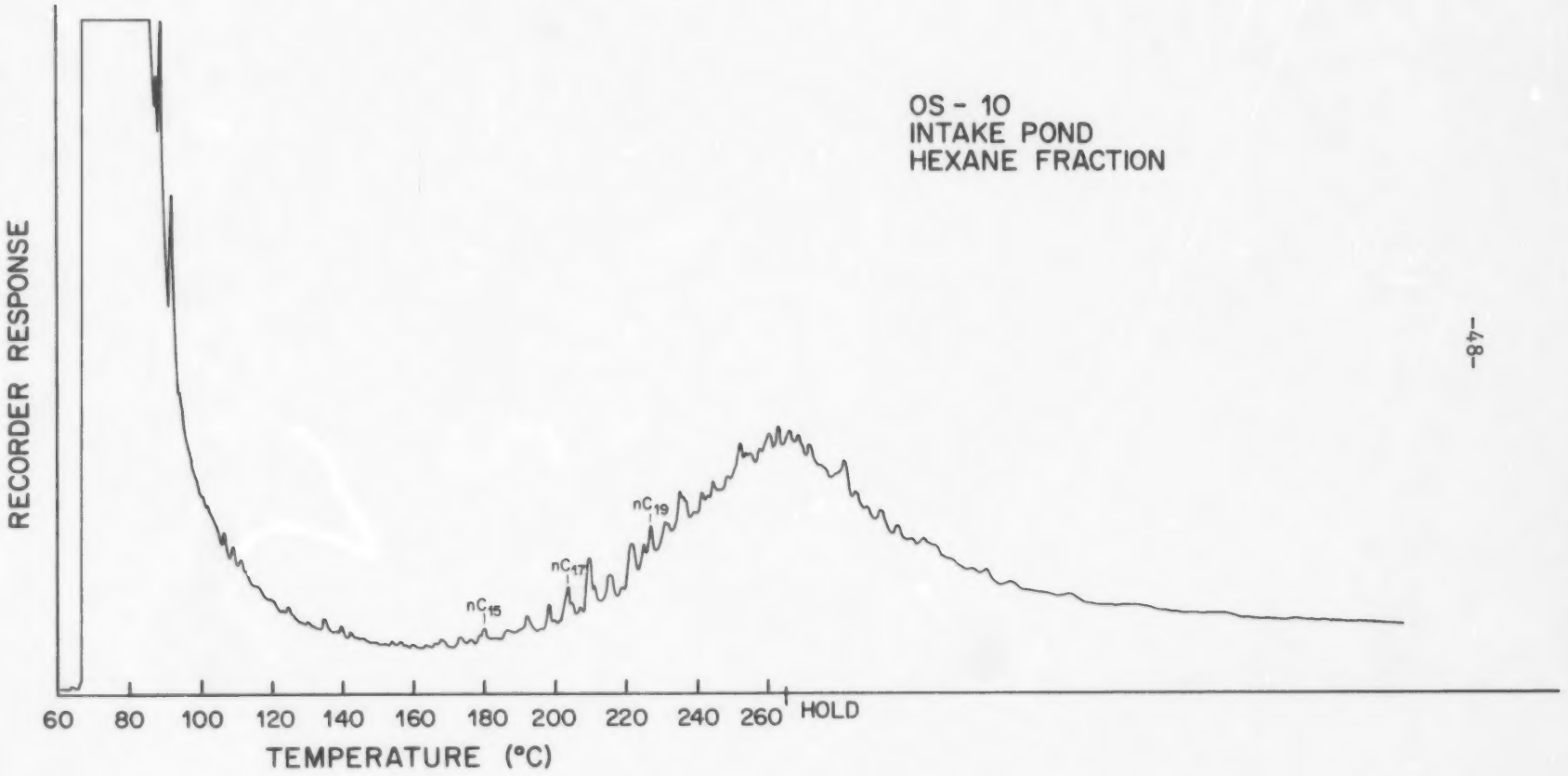
OS - 10
INTAKE POND
HEXANE FRACTION
RECORDER RESPONSE
nC15
nC17
nC19
60 80 100 120 140 160 180 200 220 240 260 HOLD
TEMPERATURE (°C)

Figure 3

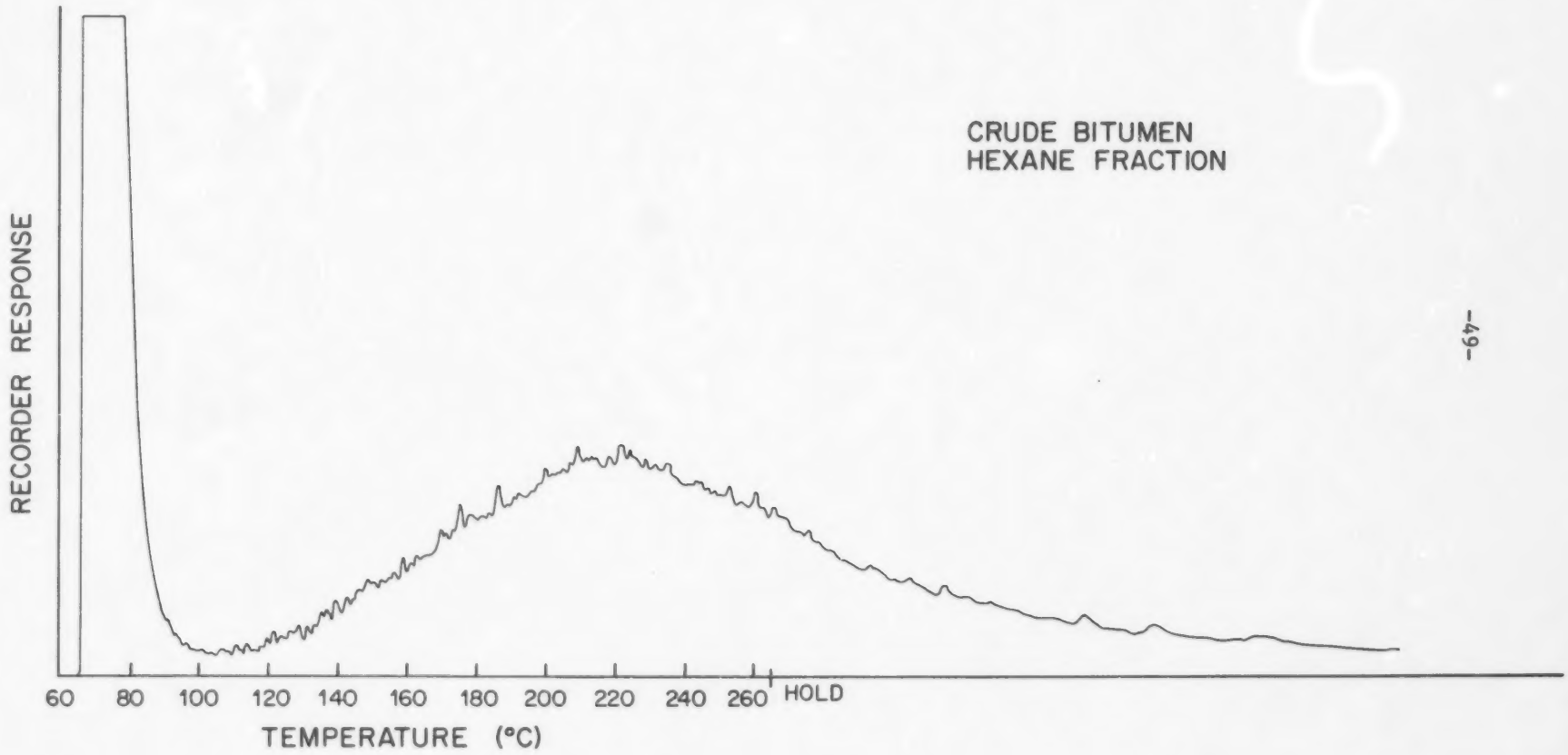
CRUDE BITUMEN
HEXANE FRACTION
RECORDER RESPONSE
60
80
100
120
140
160
180
200
220
240
260
HOLD
TEMPERATURE (°C)

Figure 4

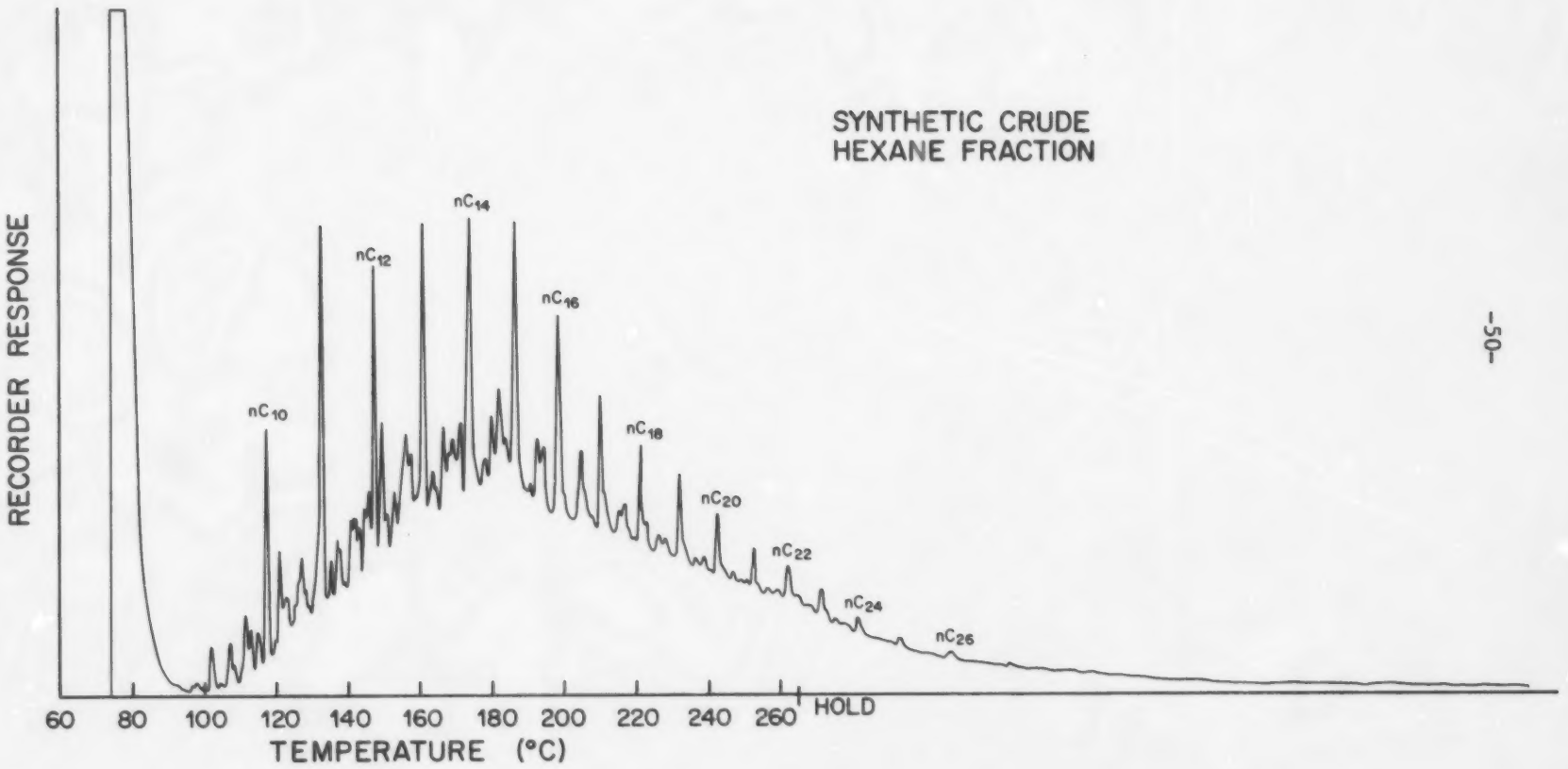
SYNTHETIC CRUDE
HEXANE FRACTION
RECORDER RESPONSE
nC10
nC12
nC14
nC16
nC18
nC20
nC22
nC24
nC26
60
80
100
120
140
160
180
200
220
240
260
HOLD
TEMPERATURE (°C)

Figure 5

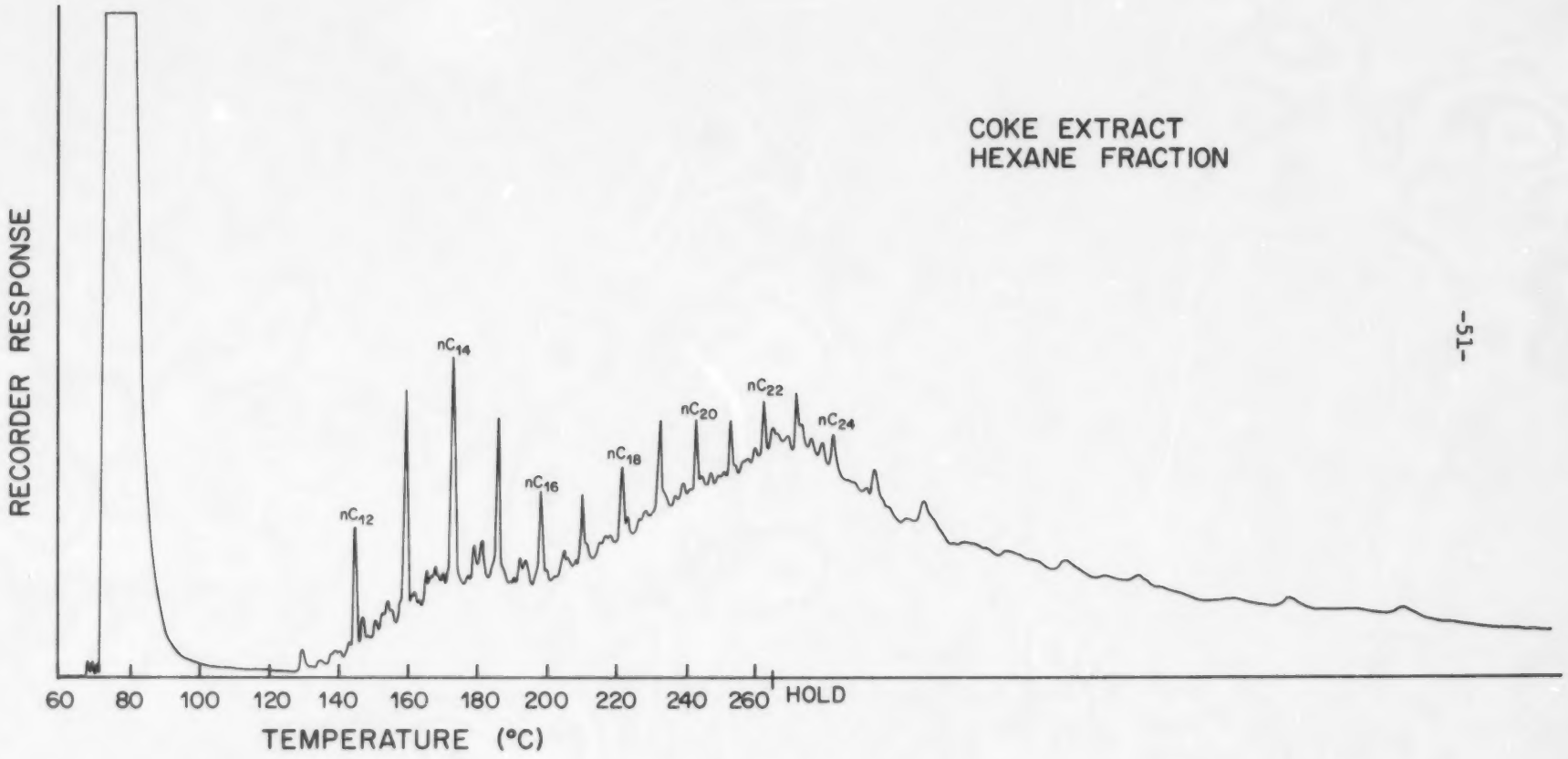
COKE EXTRACT
HEXANE FRACTION
RECORDER RESPONSE
nC12
nC14
nC16
nC18
nC20
nC22
nC24
60
80
100
120
140
160
180
200
220
240
260
HOLD
TEMPERATURE (°C)

Figure 6

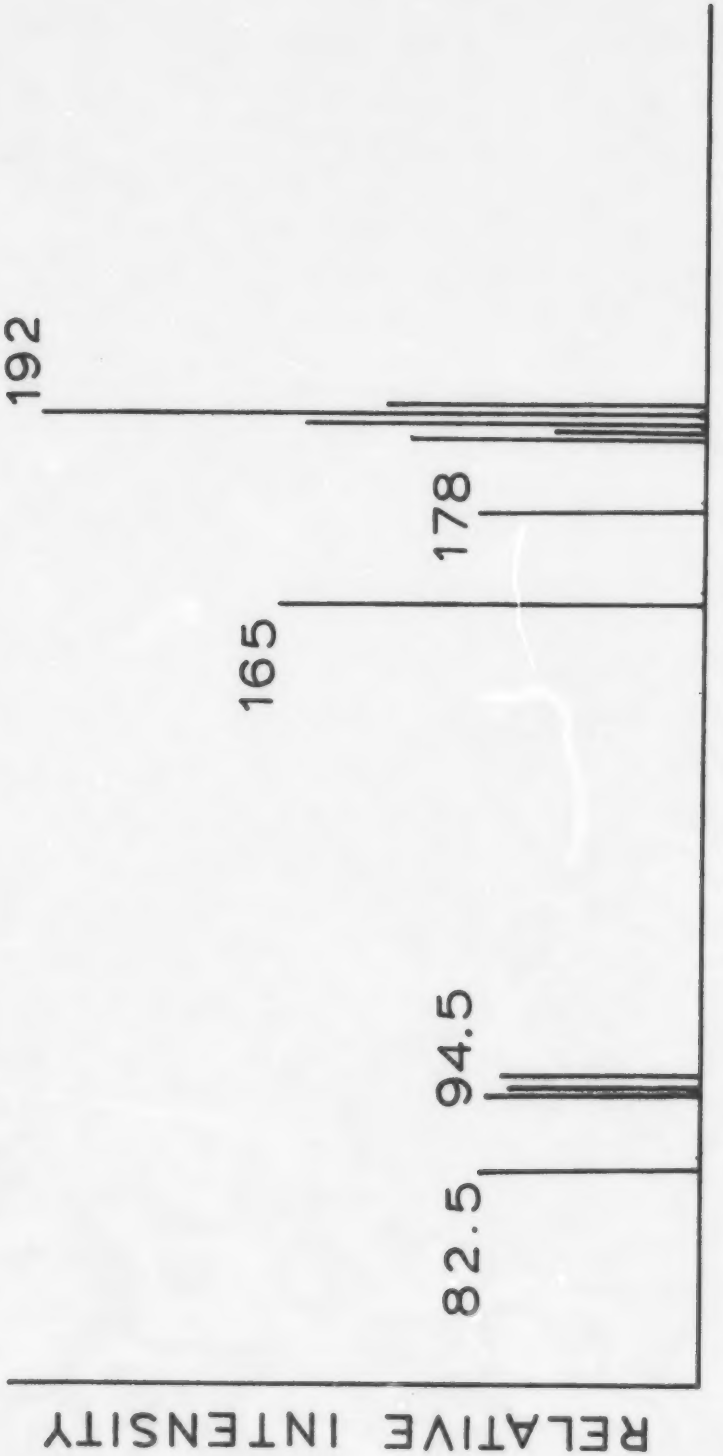

Figure 7

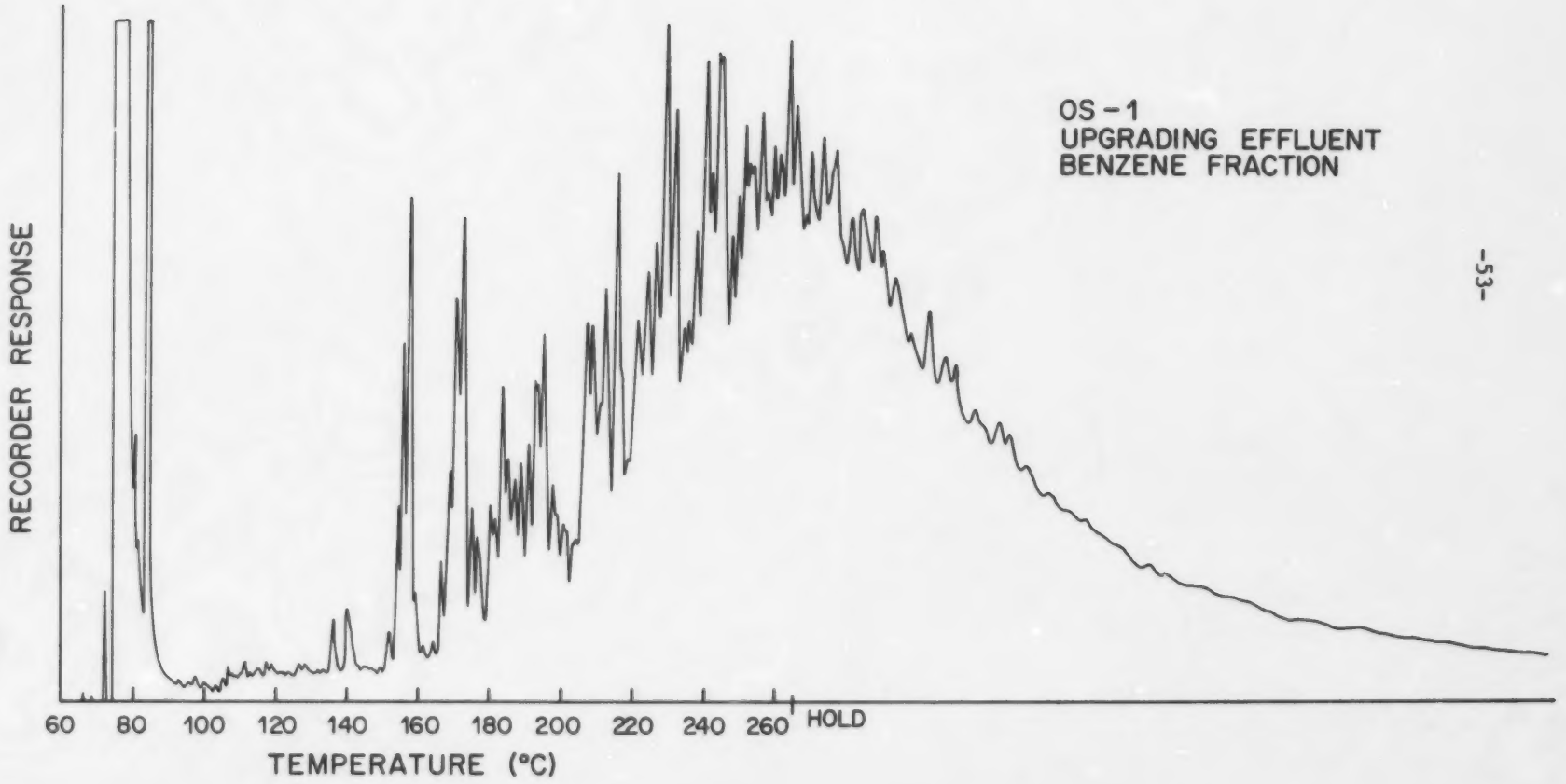
OS-1
UPGRADING EFFLUENT
BENZENE FRACTION
RECORDER RESPONSE
60
80
100
120
140
160
180
200
220
240
260
HOLD
TEMPERATURE (°C)

Figure 8

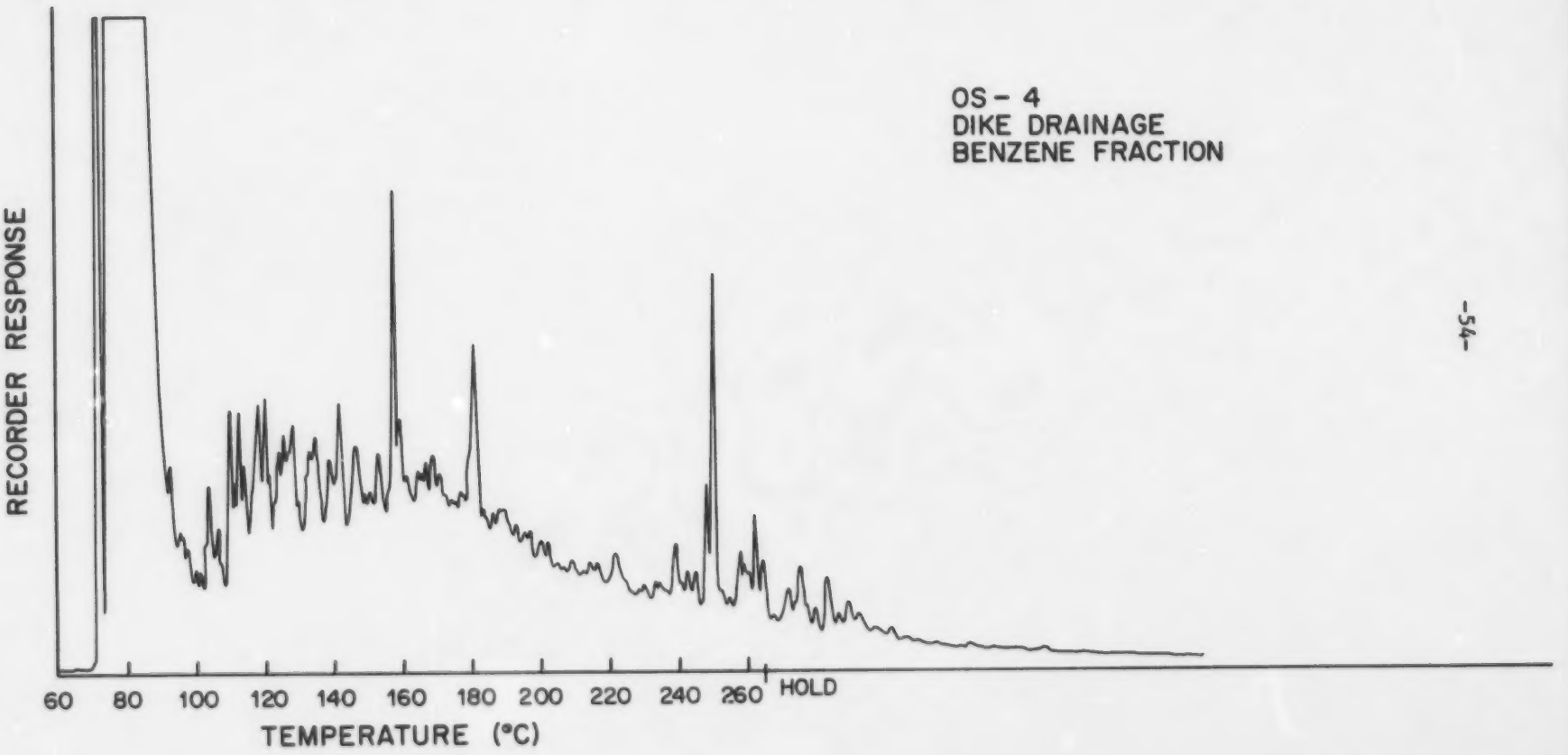
OS - 4
DIKE DRAINAGE
BENZENE FRACTION
RECORDER RESPONSE
60
80
100
120
140
160
180
200
220
240
260
HOLD
TEMPERATURE (°C)

Figure 9

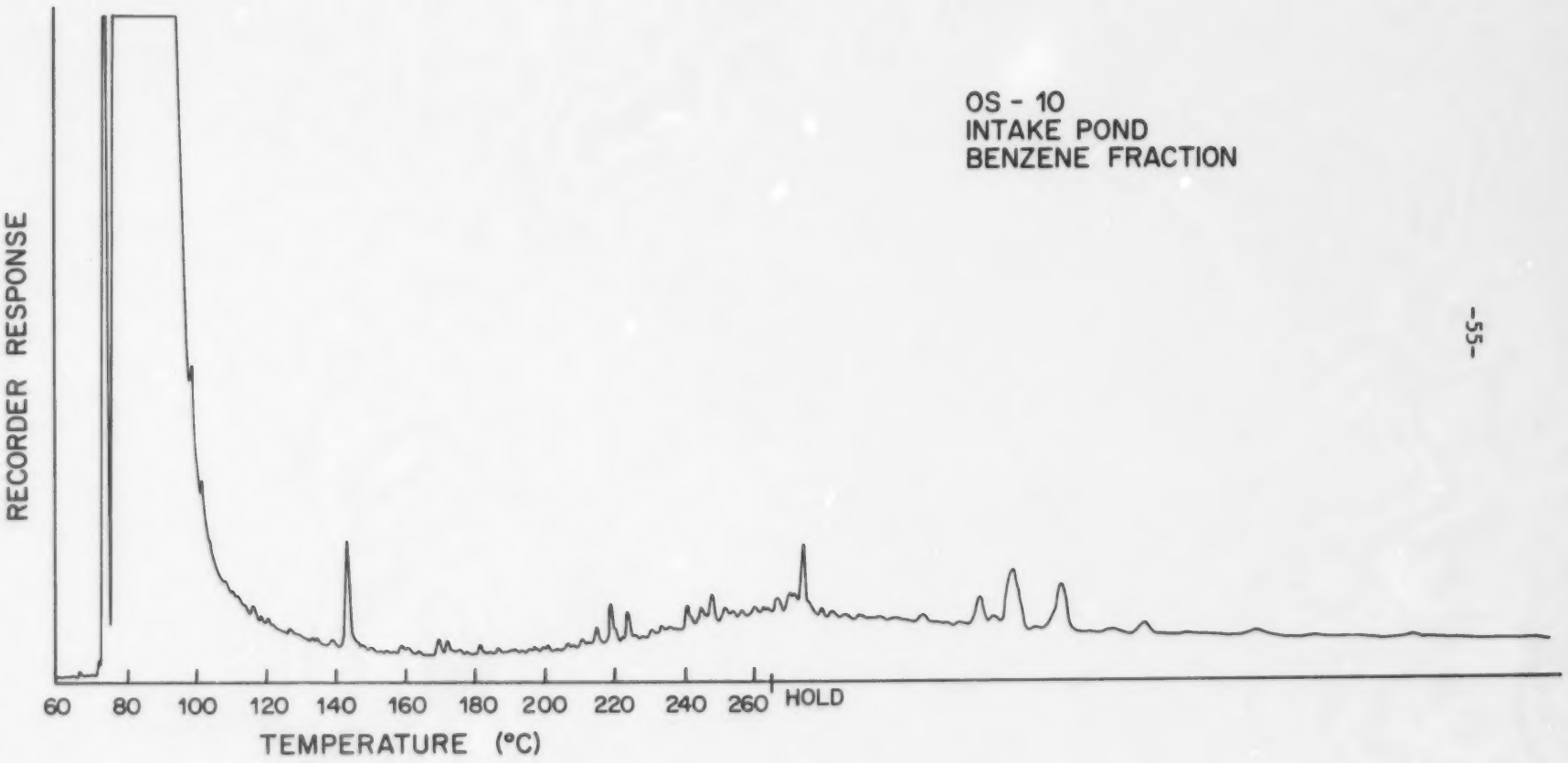
OS - 10
INTAKE POND
BENZENE FRACTION
RECORDER RESPONSE
60
80
100
120
140
160
180
200
220
240
260
HOLD
TEMPERATURE (°C)

Figure 10

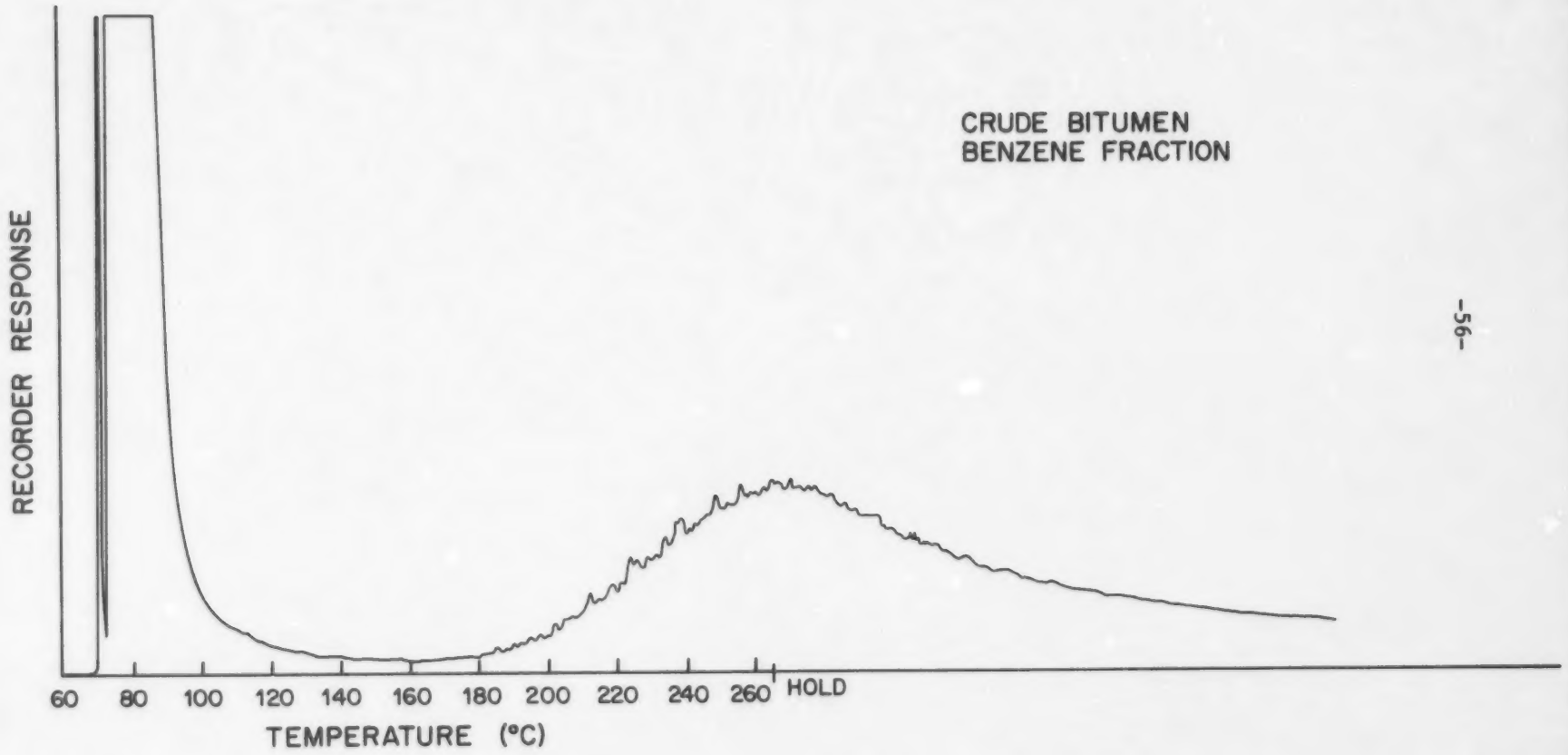
CRUDE BITUMEN
BENZENE FRACTION
RECORDER RESPONSE
60
80
100
120
140
160
180
200
220
240
260
HOLD
TEMPERATURE (°C)

Figure 11

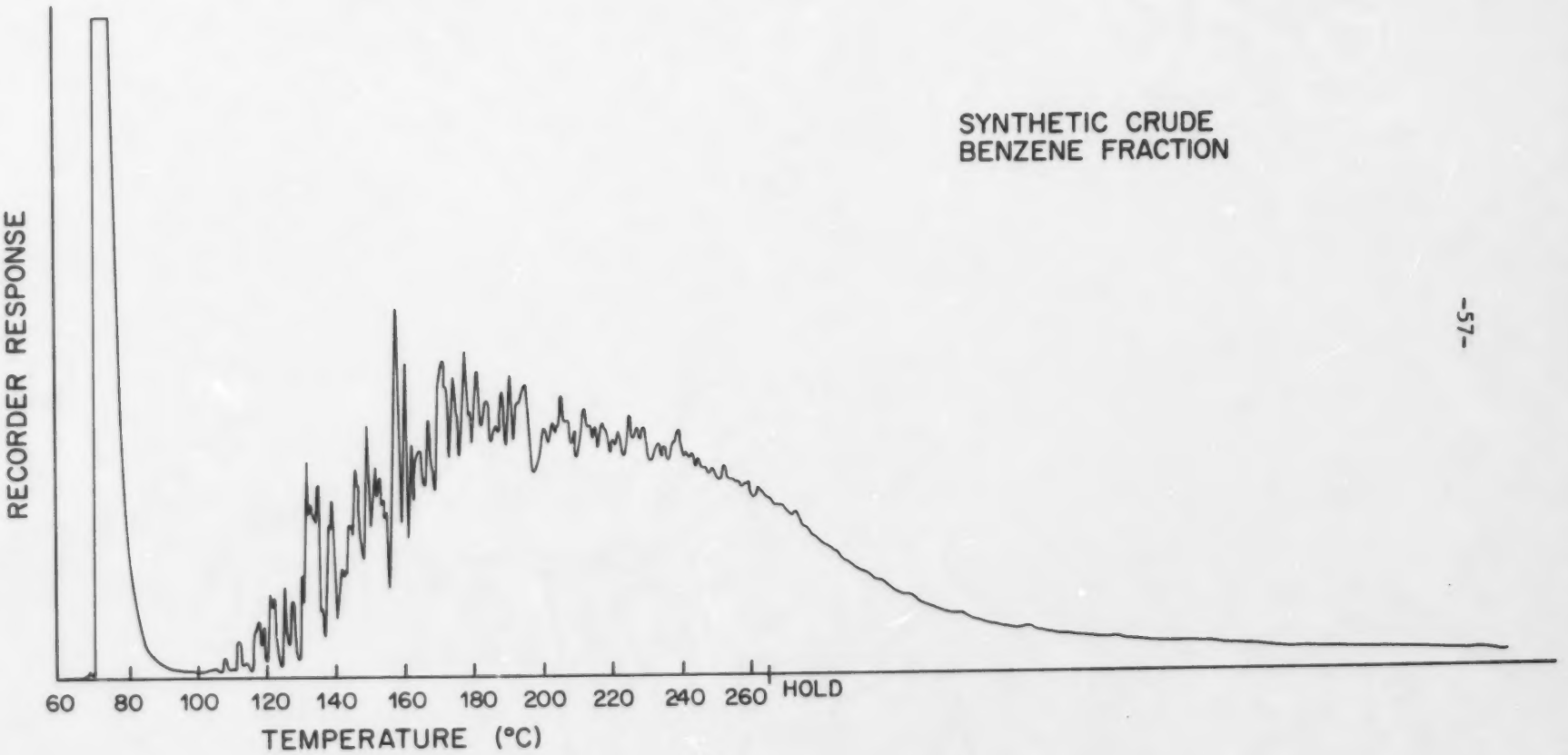
SYNTHETIC CRUDE
BENZENE FRACTION
RECORDER RESPONSE
60
80
100
120
140
160
180
200
220
240
260
HOLD
TEMPERATURE (°C)

Figure 12

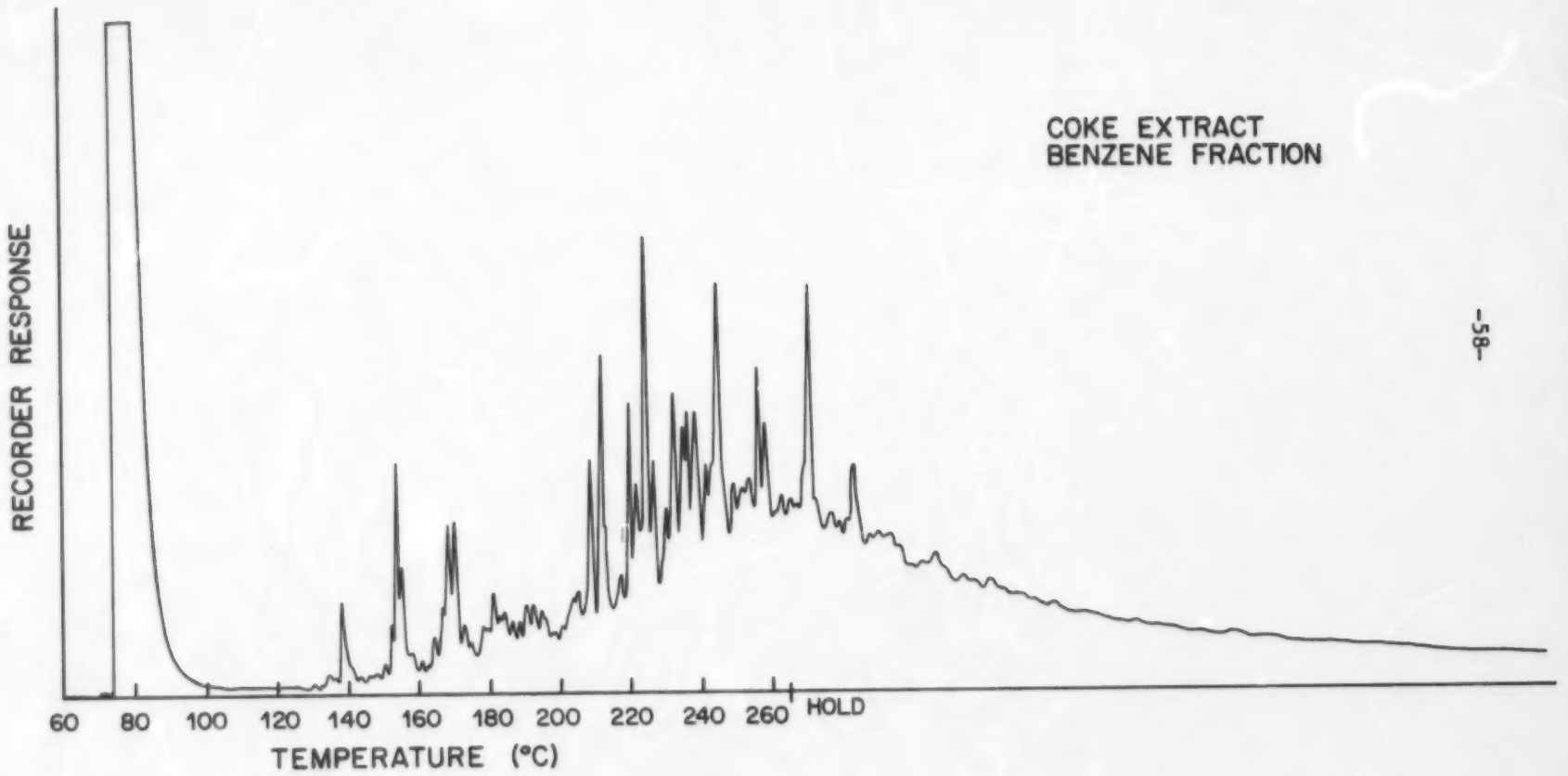
COKE EXTRACT
BENZENE FRACTION
RECORDER RESPONSE
60
80
100
120
140
160
180
200
220
240
260
HOLD
TEMPERATURE (°C)

Figure 13

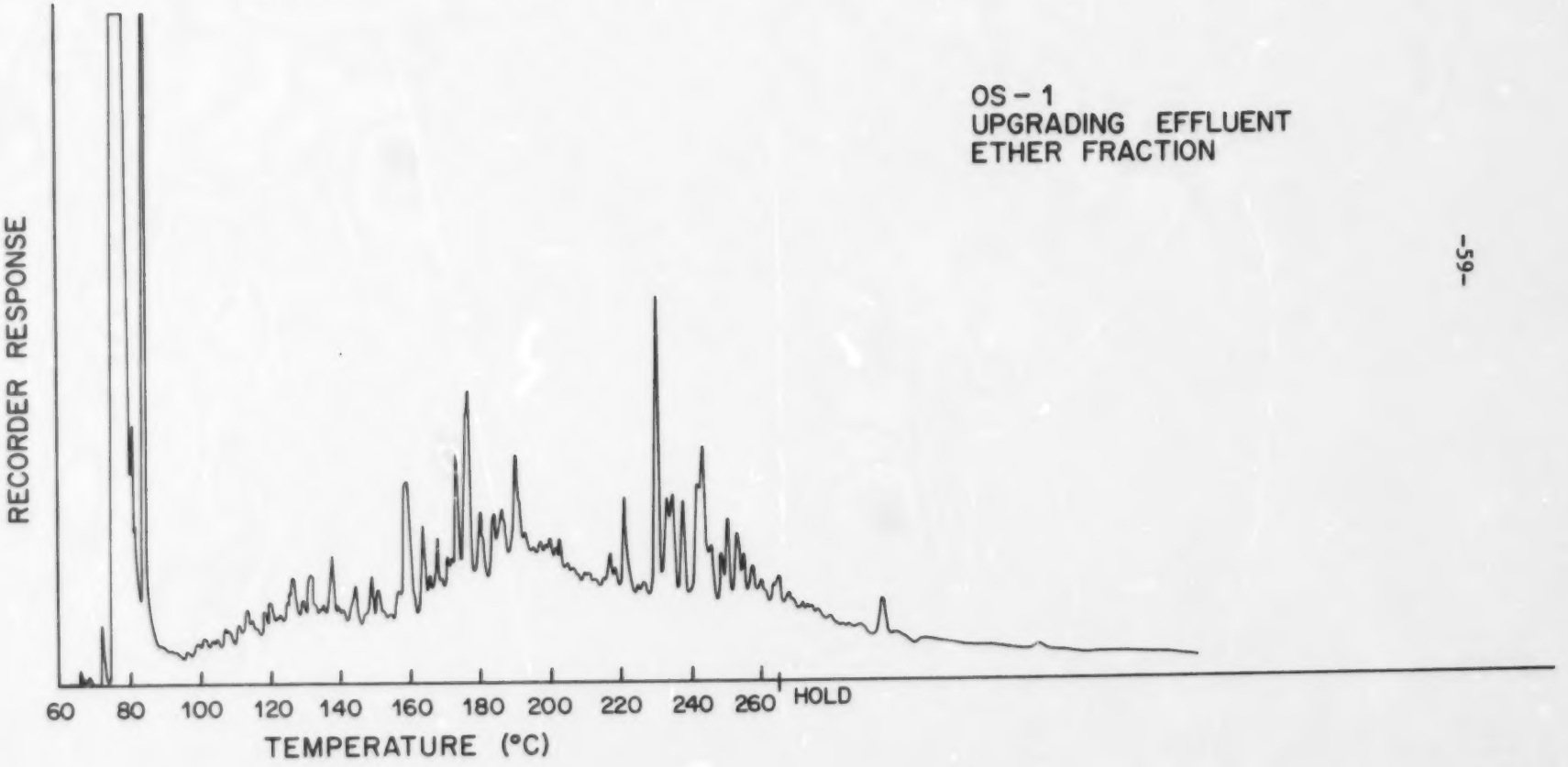
OS – 1
UPGRADING EFFLUENT
ETHER FRACTION
RECORDER RESPONSE
60 80 100 120 140 160 180 200 220 240 260 HOLD
TEMPERATURE (°C)

Figure 14

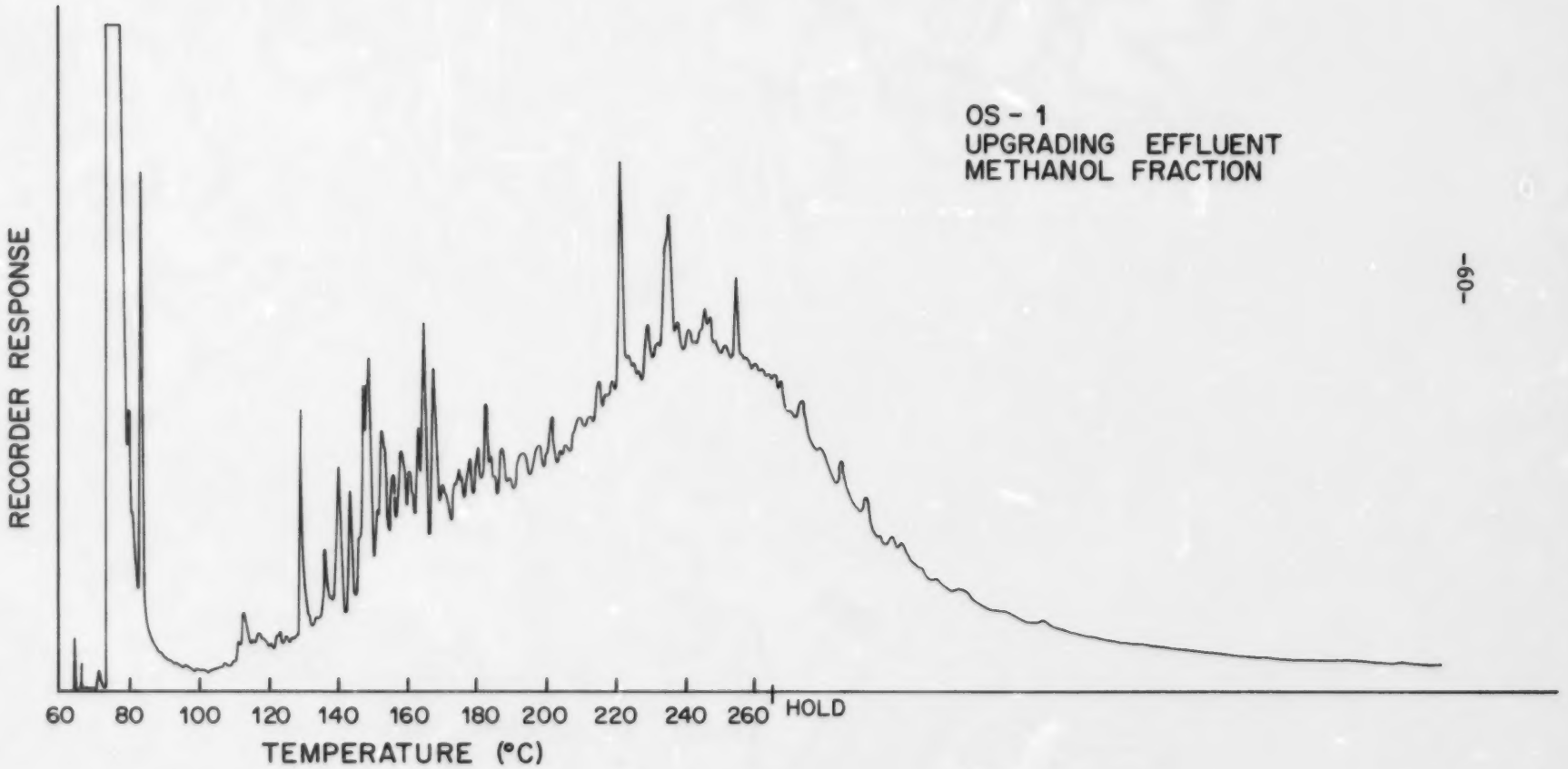
OS - 1
UPGRADING EFFLUENT
METHANOL FRACTION
RECORDER RESPONSE
60 80 100 120 140 160 180 200 220 240 260 HOLD
TEMPERATURE (°C)

Figure 15

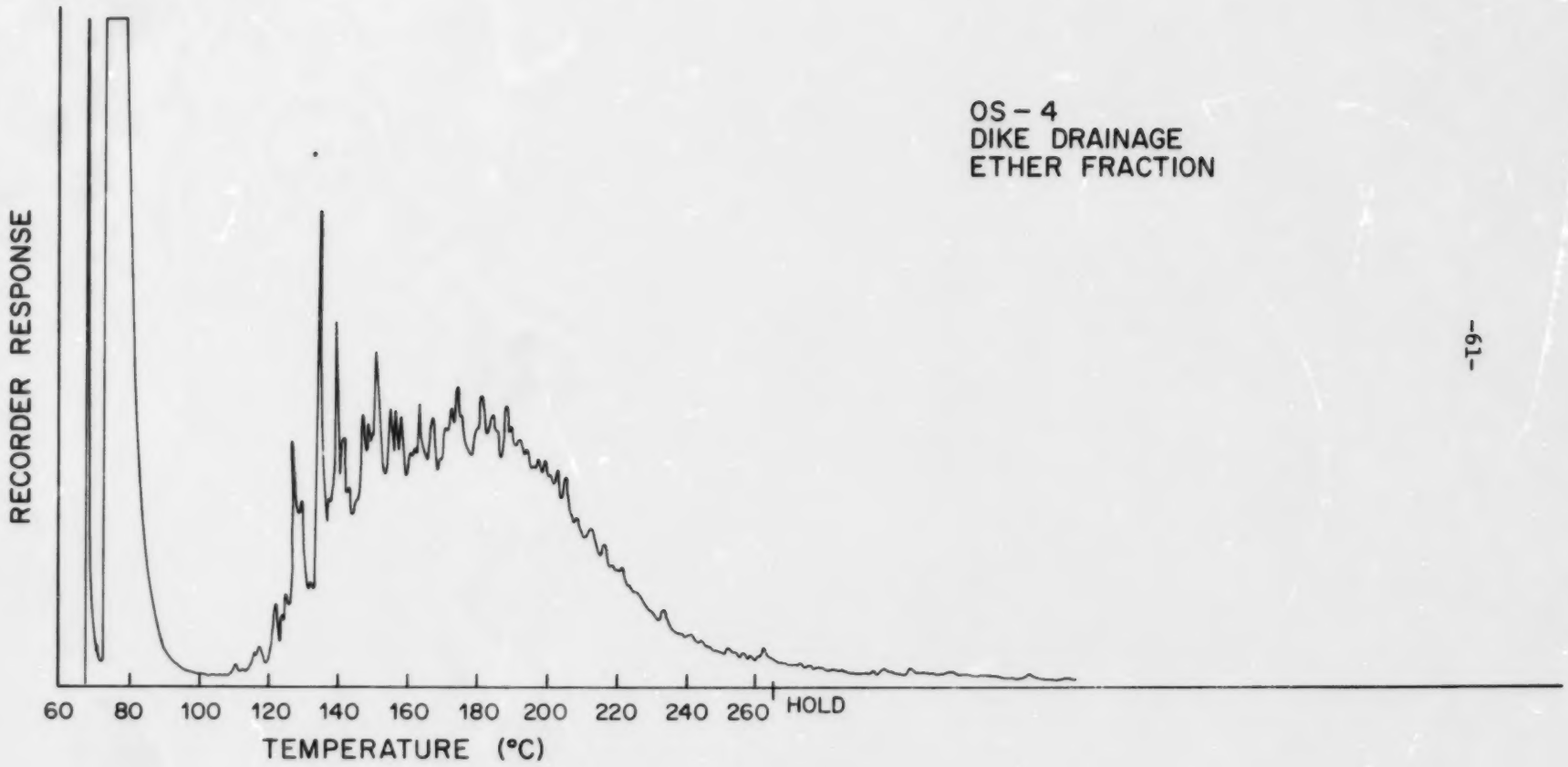
OS – 4
DIKE DRAINAGE
ETHER FRACTION
RECORDER RESPONSE
60
80
100
120
140
160
180
200
220
240
260
HOLD
TEMPERATURE (°C)

Figure 16

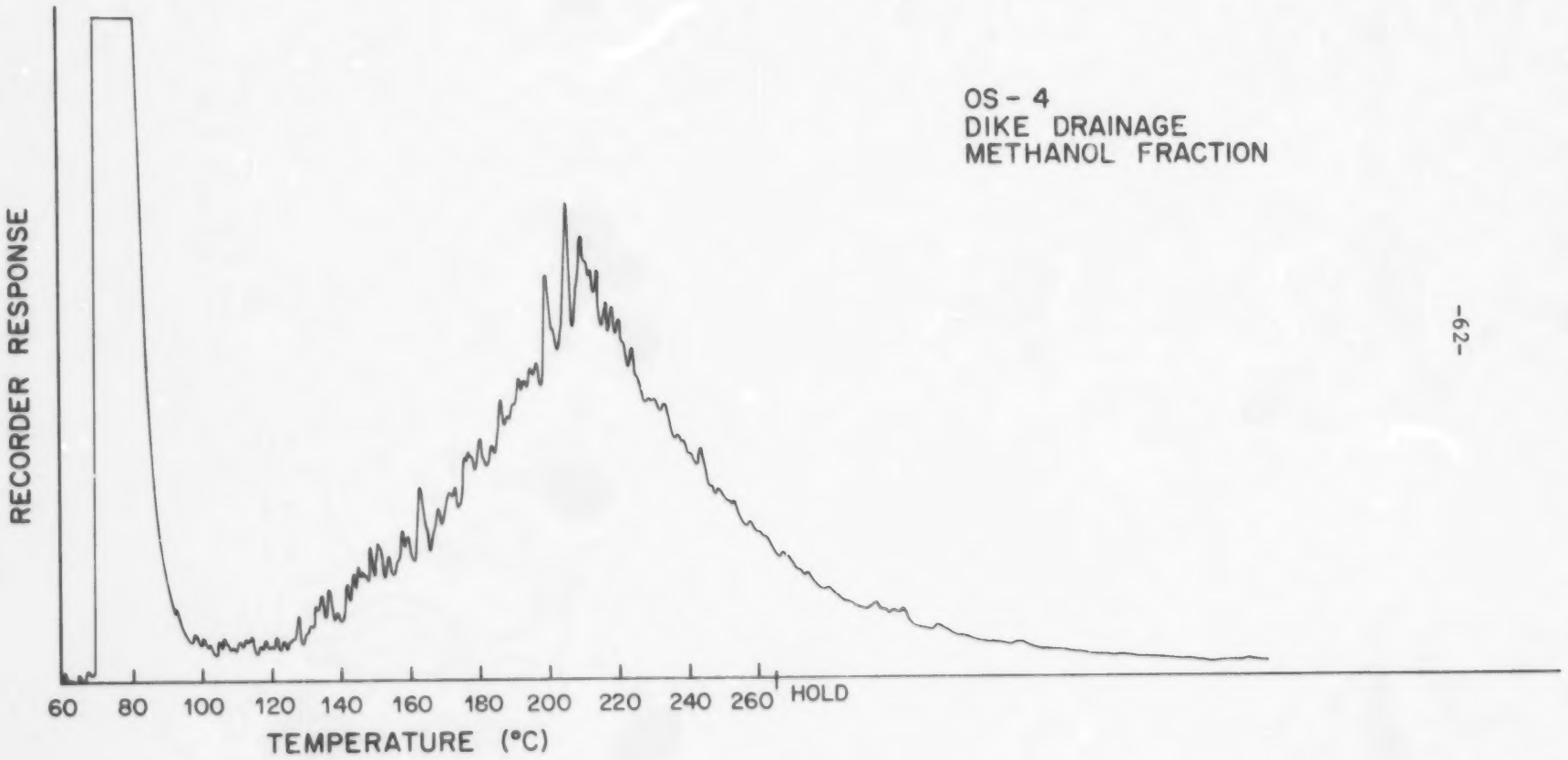
OS - 4
DIKE DRAINAGE
METHANOL FRACTION
RECORDER RESPONSE
60
80
100
120
140
160
180
200
220
240
260
HOLD
TEMPERATURE (°C)

Figure 17

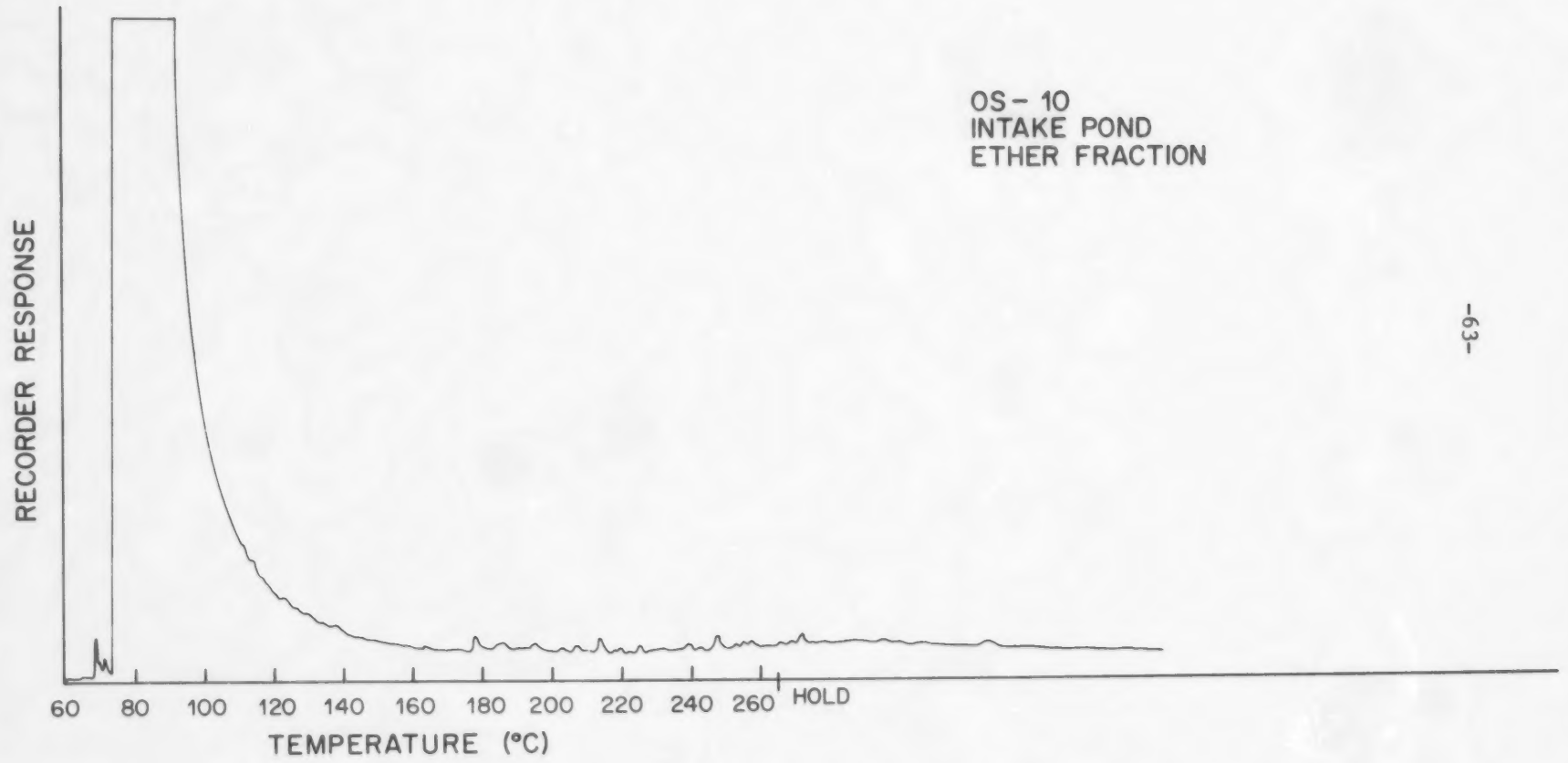
OS – 10
INTAKE POND
ETHER FRACTION
RECORDER RESPONSE
60 80 100 120 140 160 180 200 220 240 260 HOLD
TEMPERATURE (°C)

Figure 18

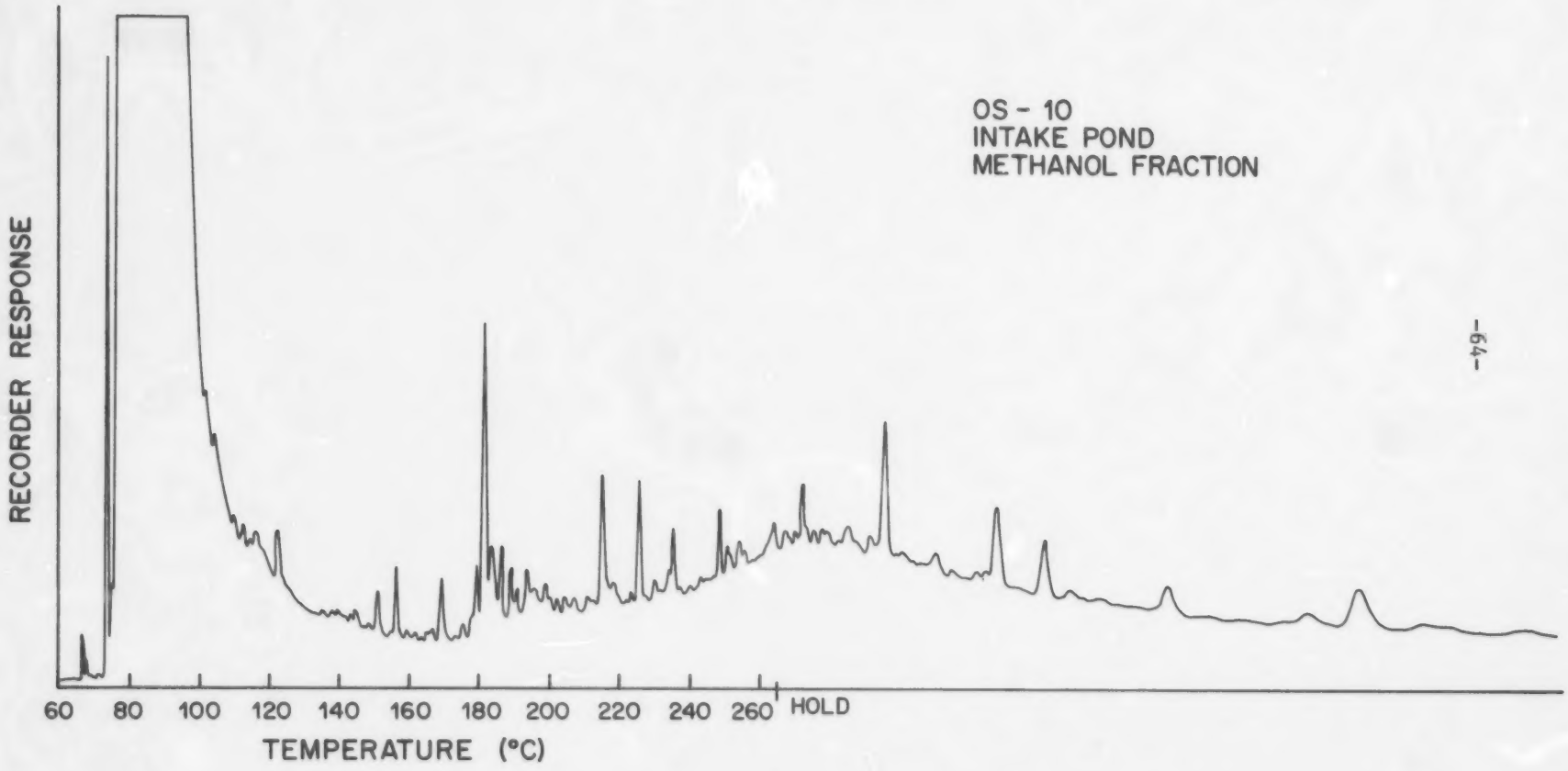
OS - 10
INTAKE POND
METHANOL FRACTION
RECORDER RESPONSE
60
80
100
120
140
160
180
200
220
240
260
HOLD
TEMPERATURE (°C)

Figure 19

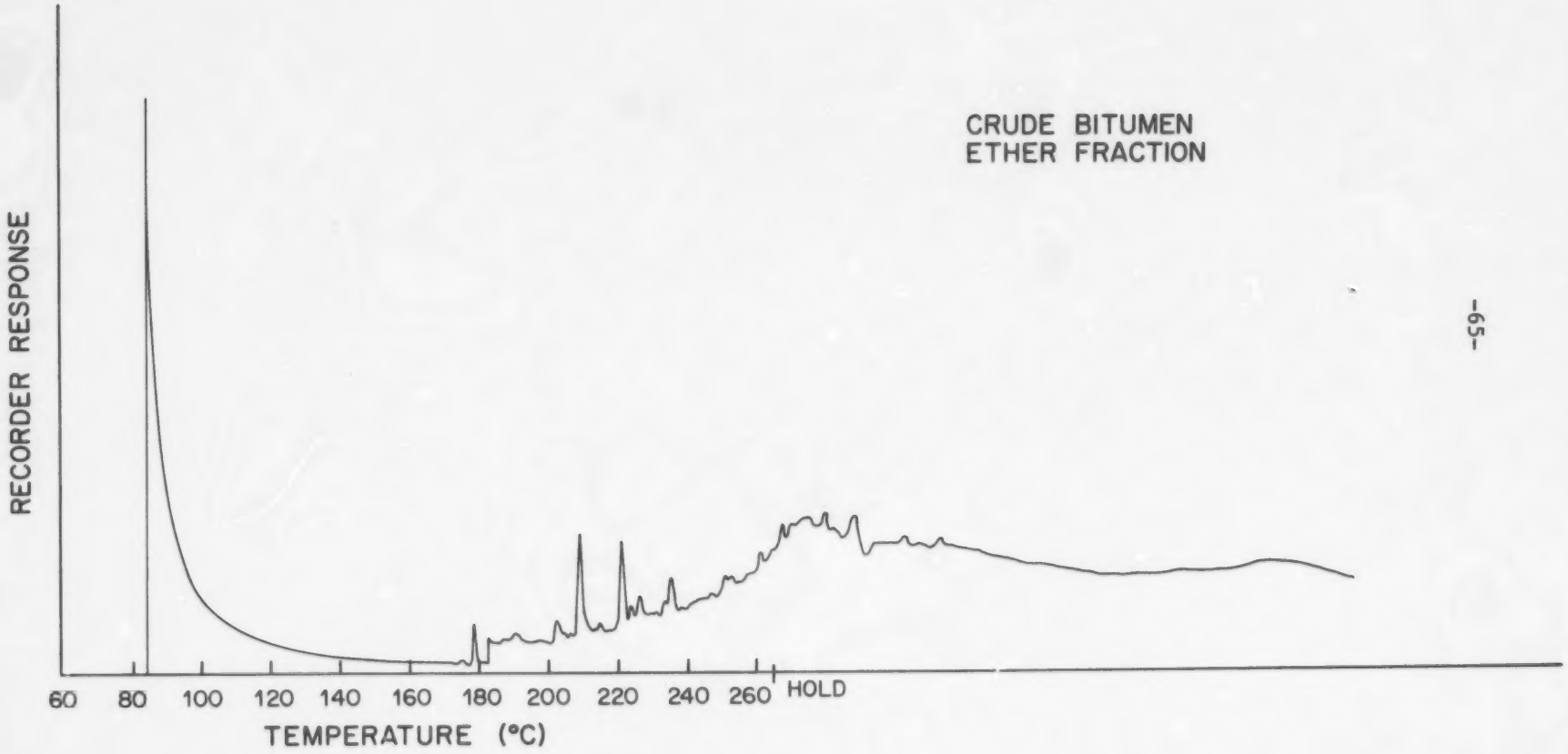
CRUDE BITUMEN
ETHER FRACTION
RECORDER RESPONSE
60
80
100
120
140
160
180
200
220
240
260
HOLD
TEMPERATURE (°C)

Figure 20

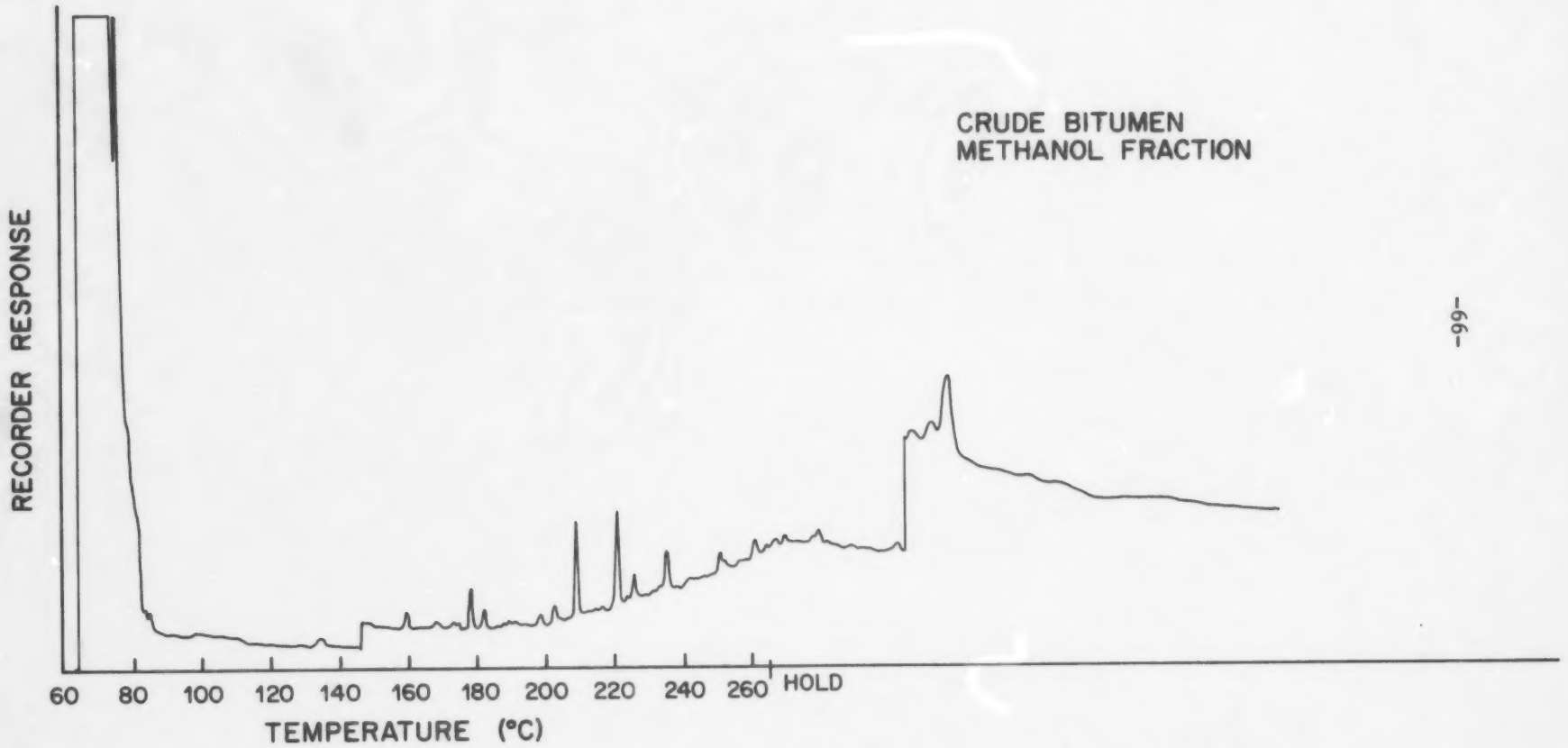
CRUDE BITUMEN
METHANOL FRACTION
RECORDER RESPONSE
60
80
100
120
140
160
180
200
220
240
260
HOLD
TEMPERATURE (°C)

Figure 21

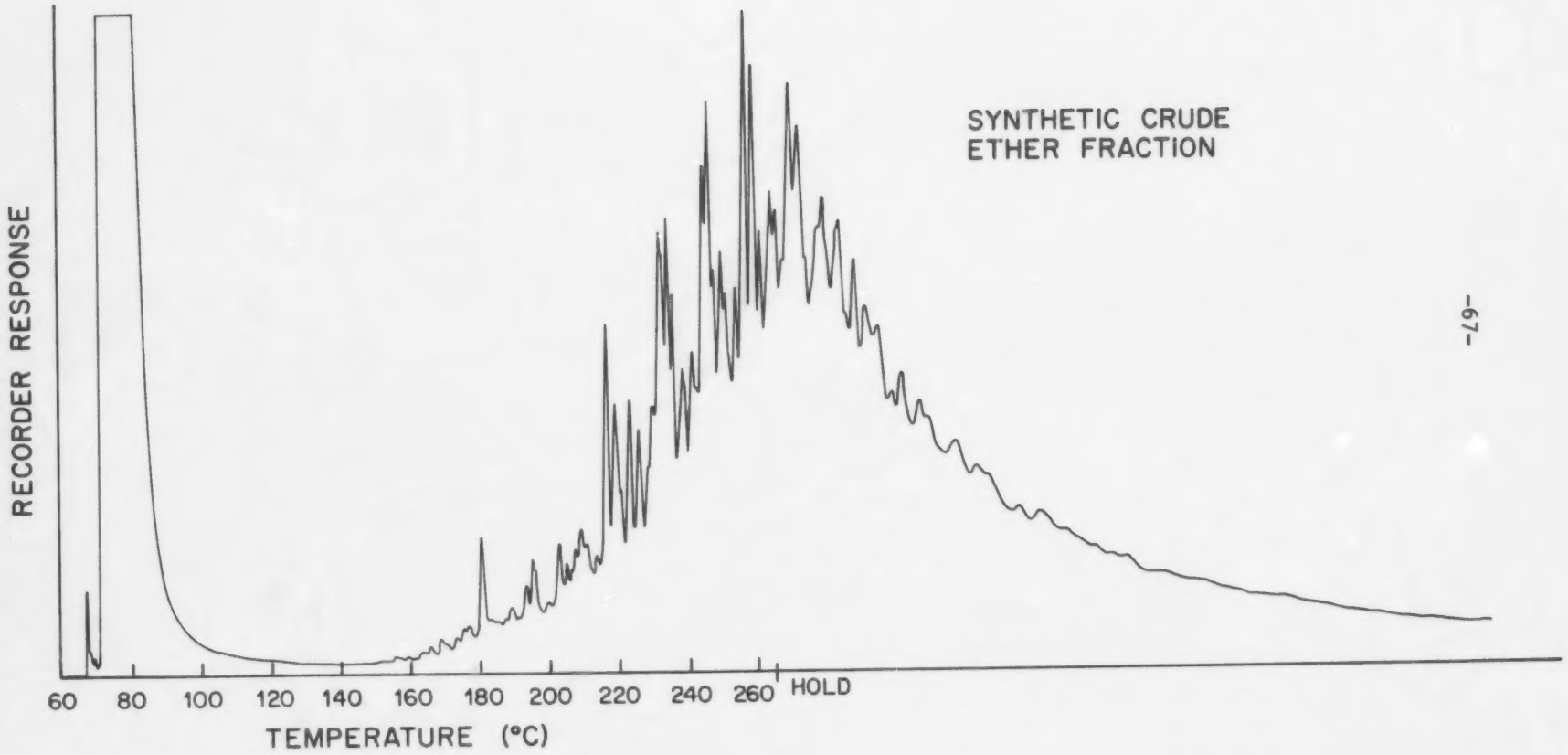
SYNTHETIC CRUDE
ETHER FRACTION
RECORDER RESPONSE
60
80
100
120
140
160
180
200
220
240
260
HOLD
TEMPERATURE (°C)

Figure 22

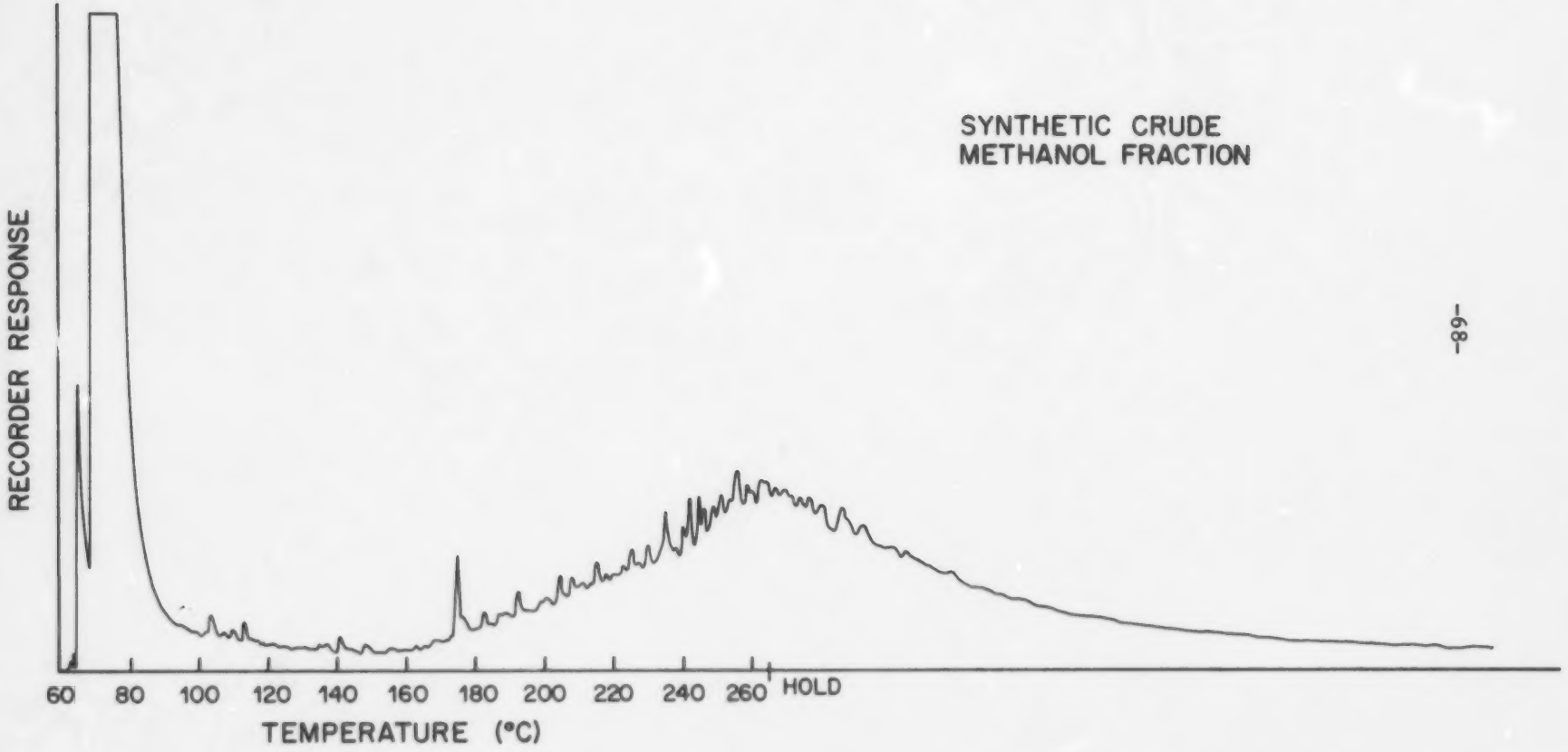
SYNTHETIC CRUDE
METHANOL FRACTION
RECORDER RESPONSE
60
80
100
120
140
160
180
200
220
240
260
HOLD
TEMPERATURE (°C)

Figure 23

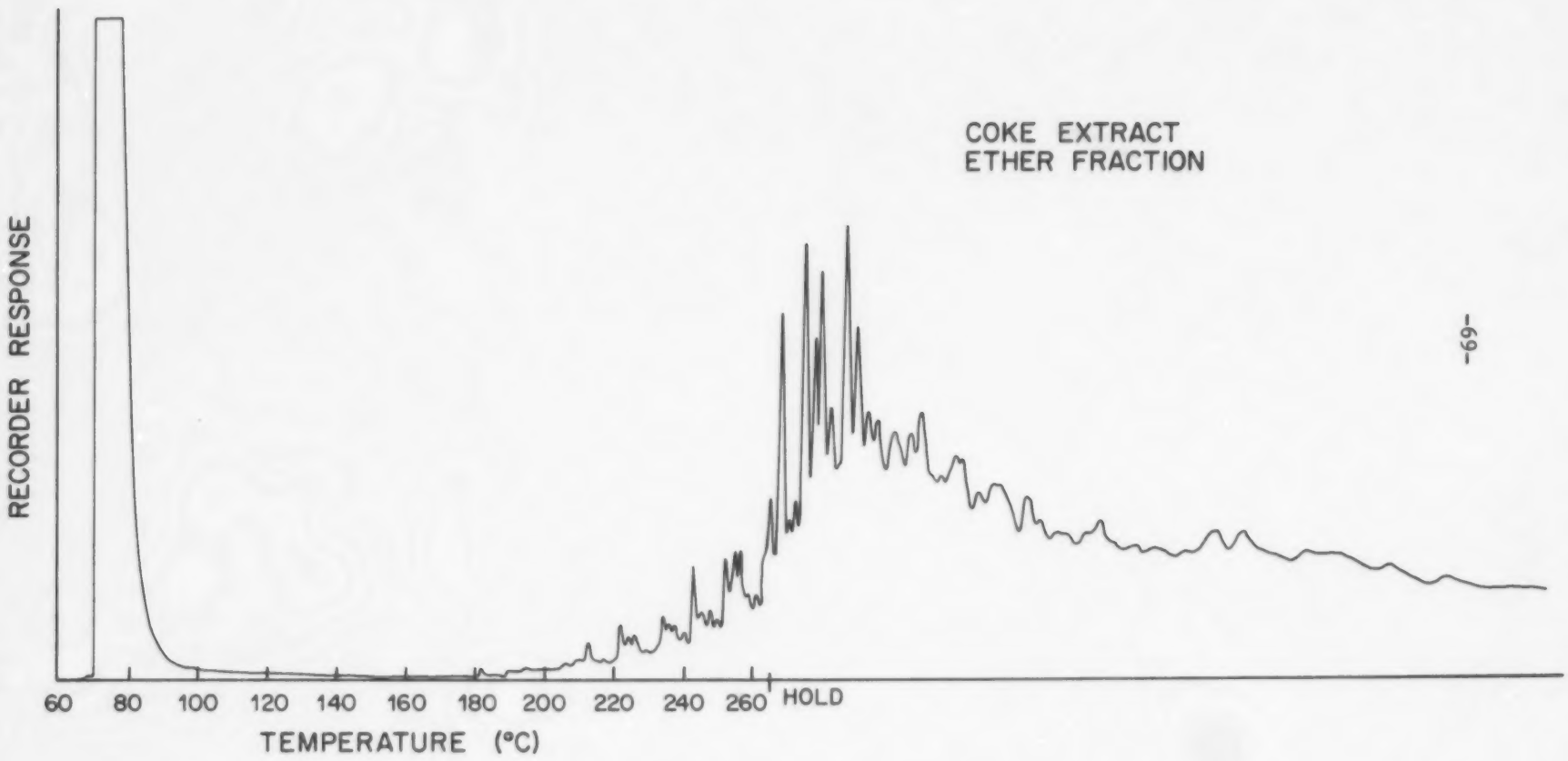
COKE EXTRACT
ETHER FRACTION
RECORDER RESPONSE
60
80
100
120
140
160
180
200
220
240
260
HOLD
TEMPERATURE (°C)

Figure 24

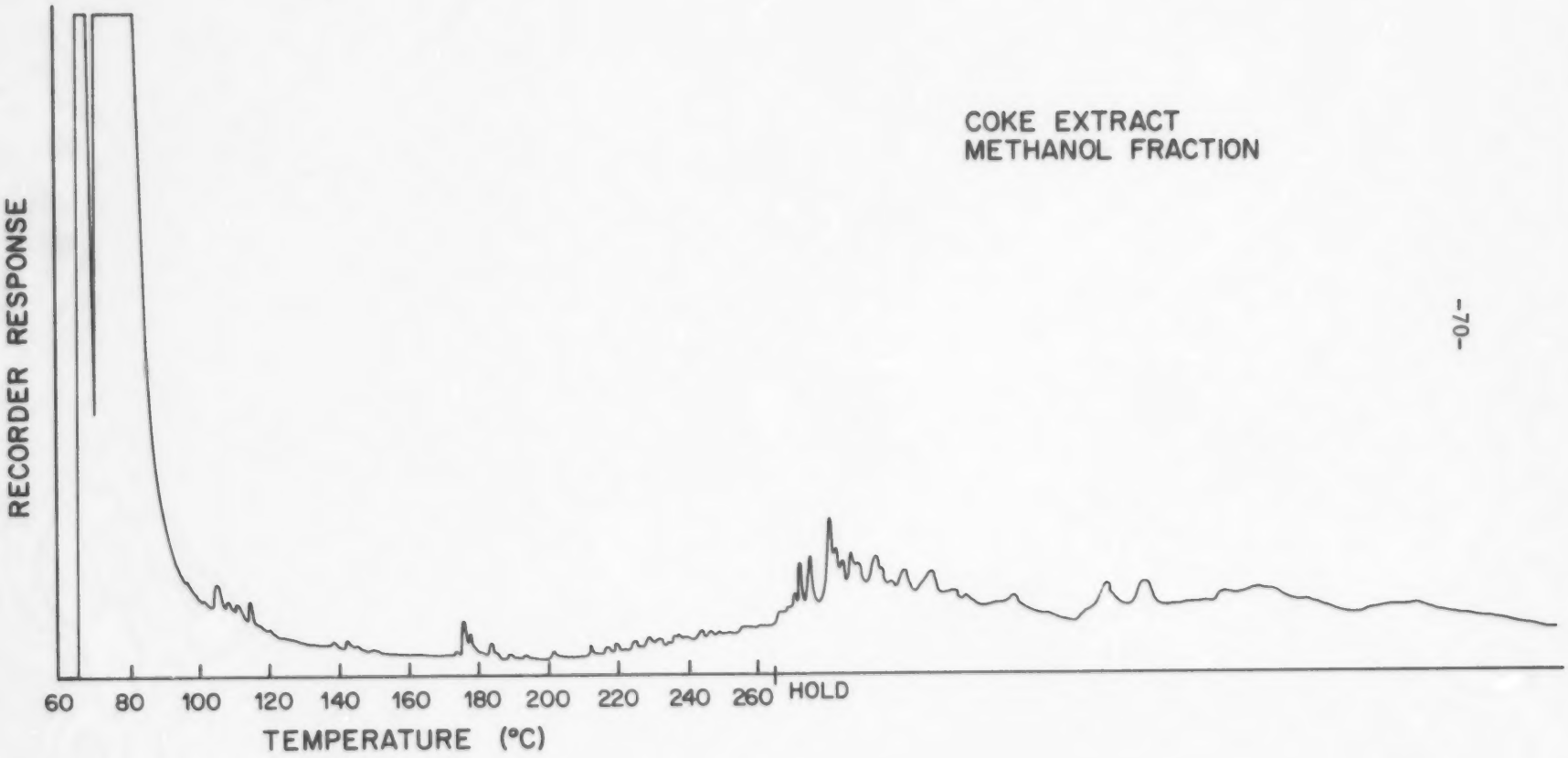
COKE EXTRACT
METHANOL FRACTION
RECORDER RESPONSE
60
80
100
120
140
160
180
200
220
240
260
HOLD
TEMPERATURE (°C)

Figure 25

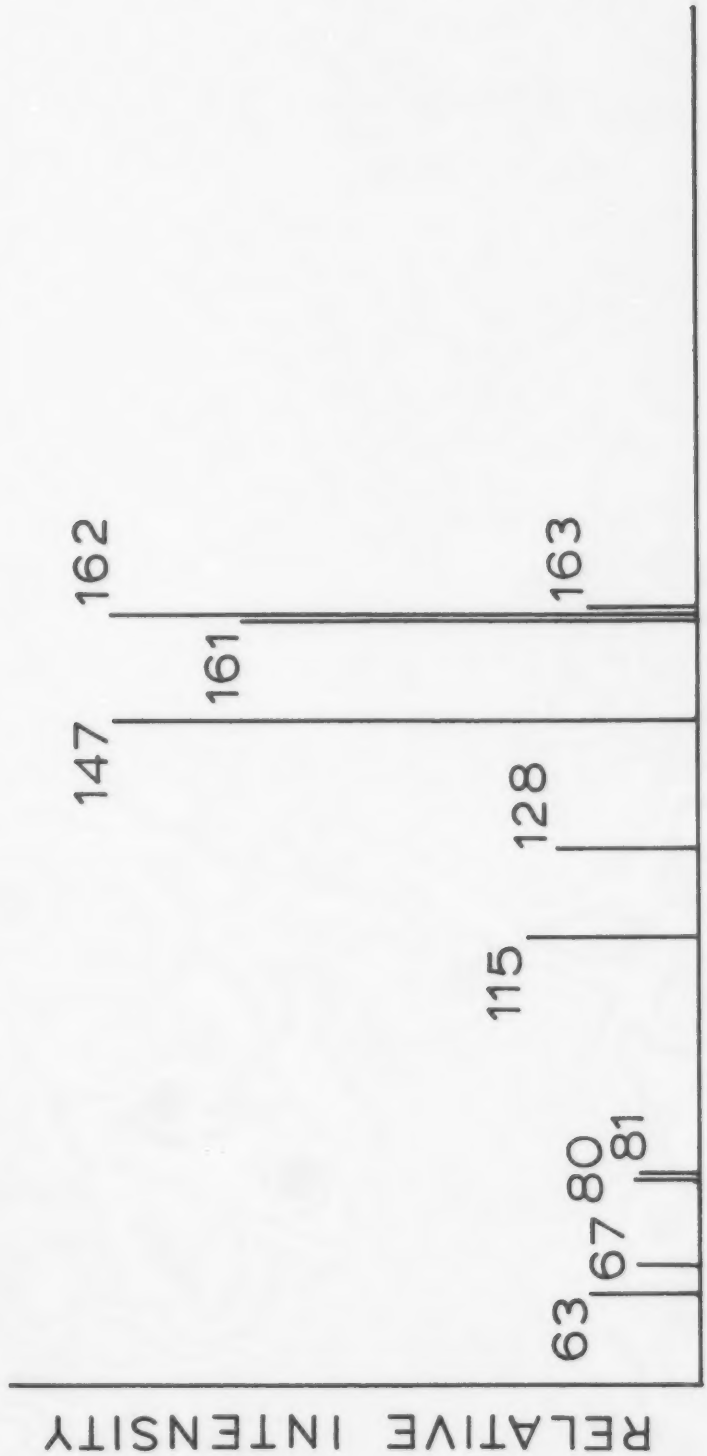

Figure 26

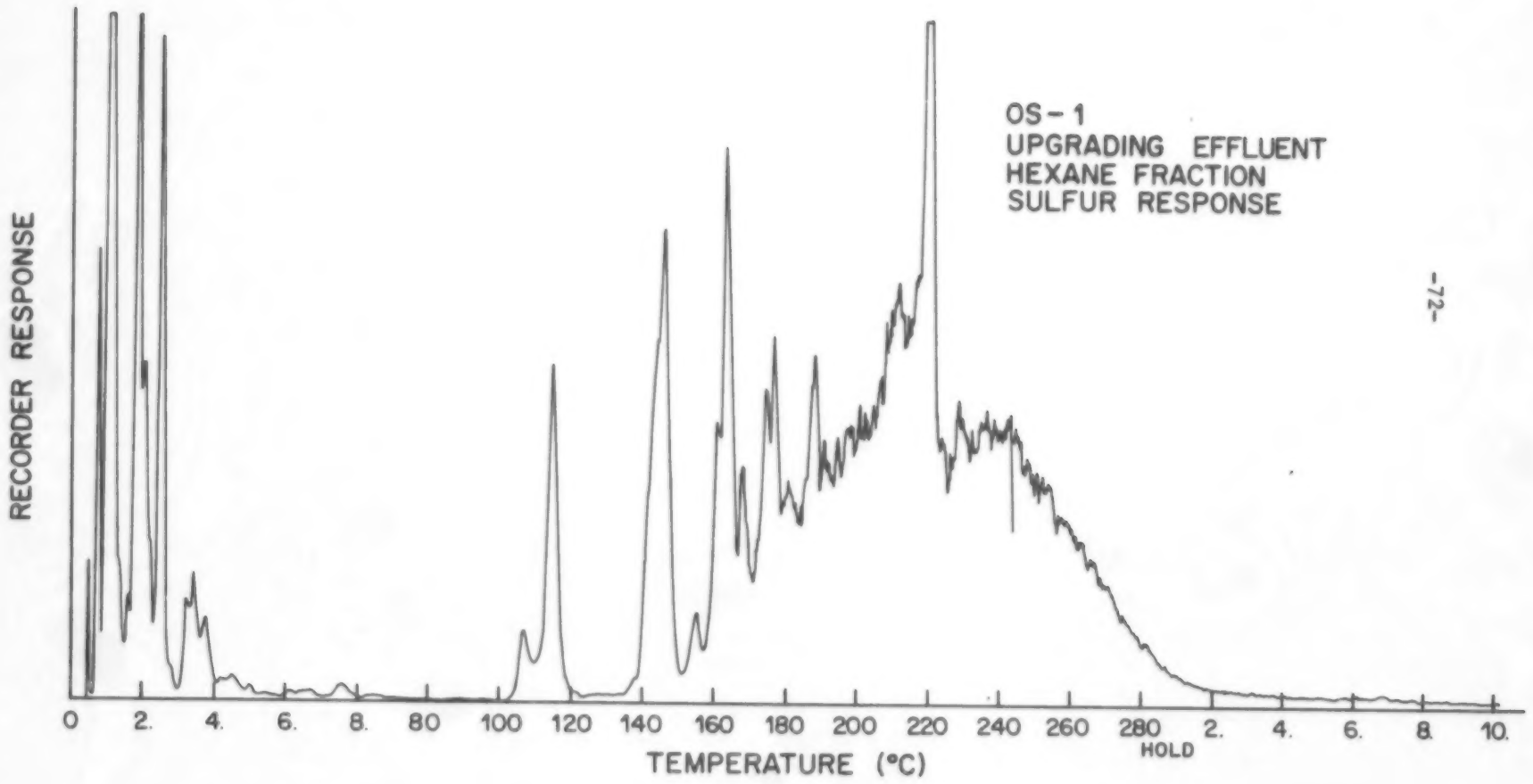
OS-1
UPGRADING EFFLUENT
HEXANE FRACTION
SULFUR RESPONSE
RECORDER RESPONSE
0 2. 4. 6. 8. 80 100 120 140 160 180 200 220 240 260 280 2. 4. 6. 8. 10.
HOLD
TEMPERATURE (°C)

Figure 27

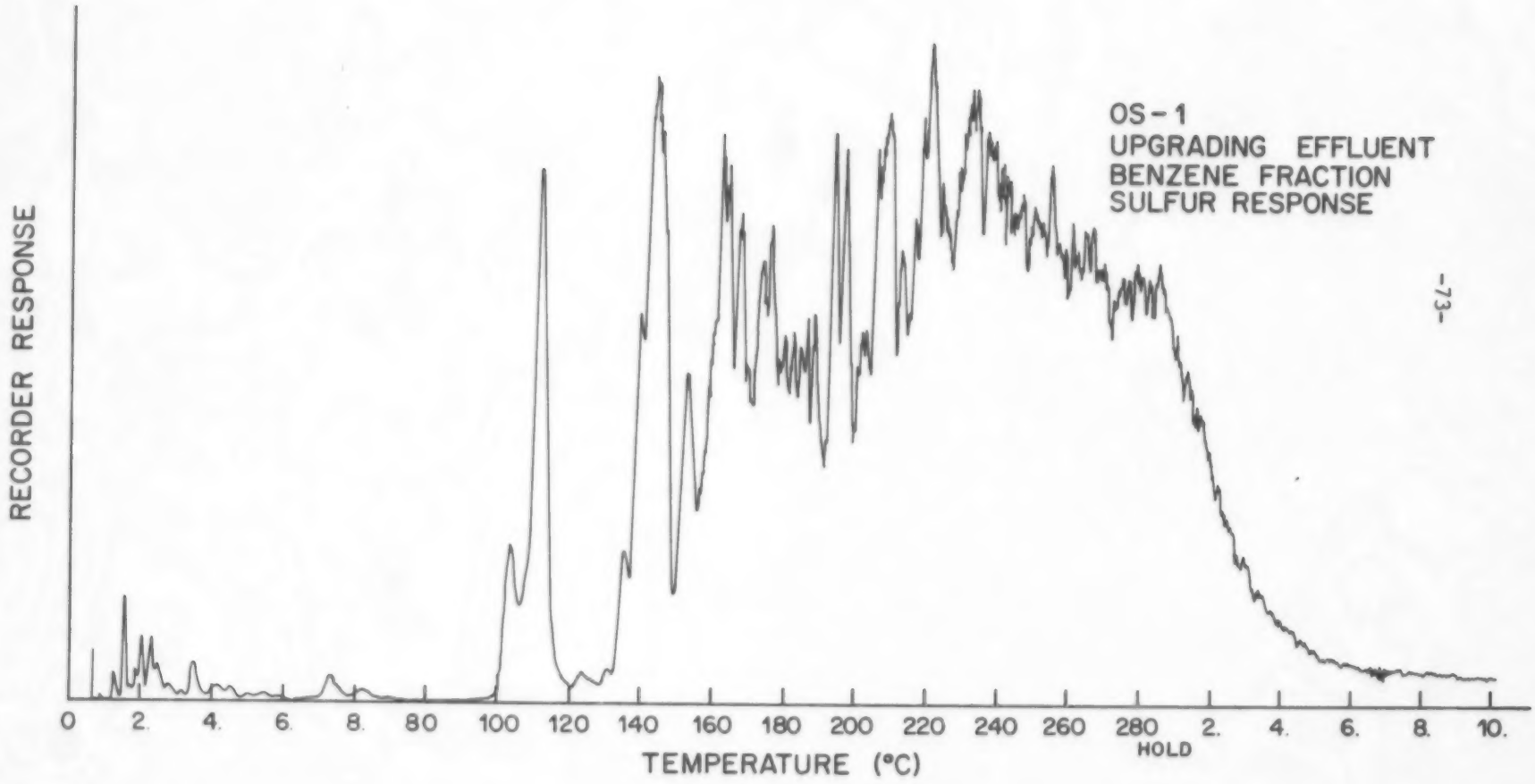
OS-1
UPGRADING EFFLUENT
BENZENE FRACTION
SULFUR RESPONSE
RECORDER RESPONSE
0 2. 4. 6. 8. 80 100 120 140 160 180 200 220 240 260 280 2. 4. 6. 8. 10.
HOLD
TEMPERATURE (°C)

Figure 28

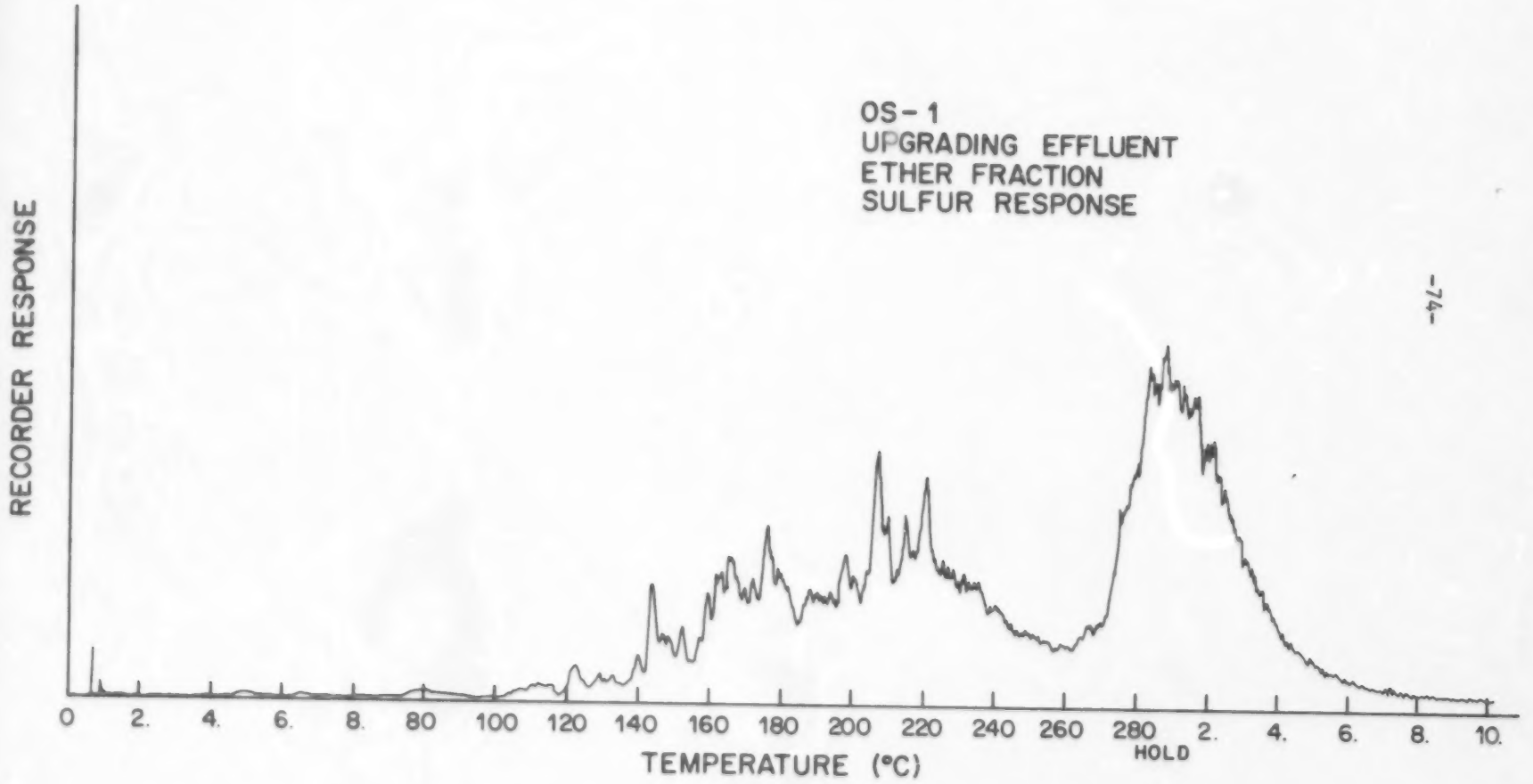
OS-1
UPGRADING EFFLUENT
ETHER FRACTION
SULFUR RESPONSE
RECORDER RESPONSE
0
2.
4.
6.
8.
80
100
120
140
160
180
200
220
240
260
280
2.
4.
6.
8.
10.
HOLD
TEMPERATURE (°C)

Figure 29

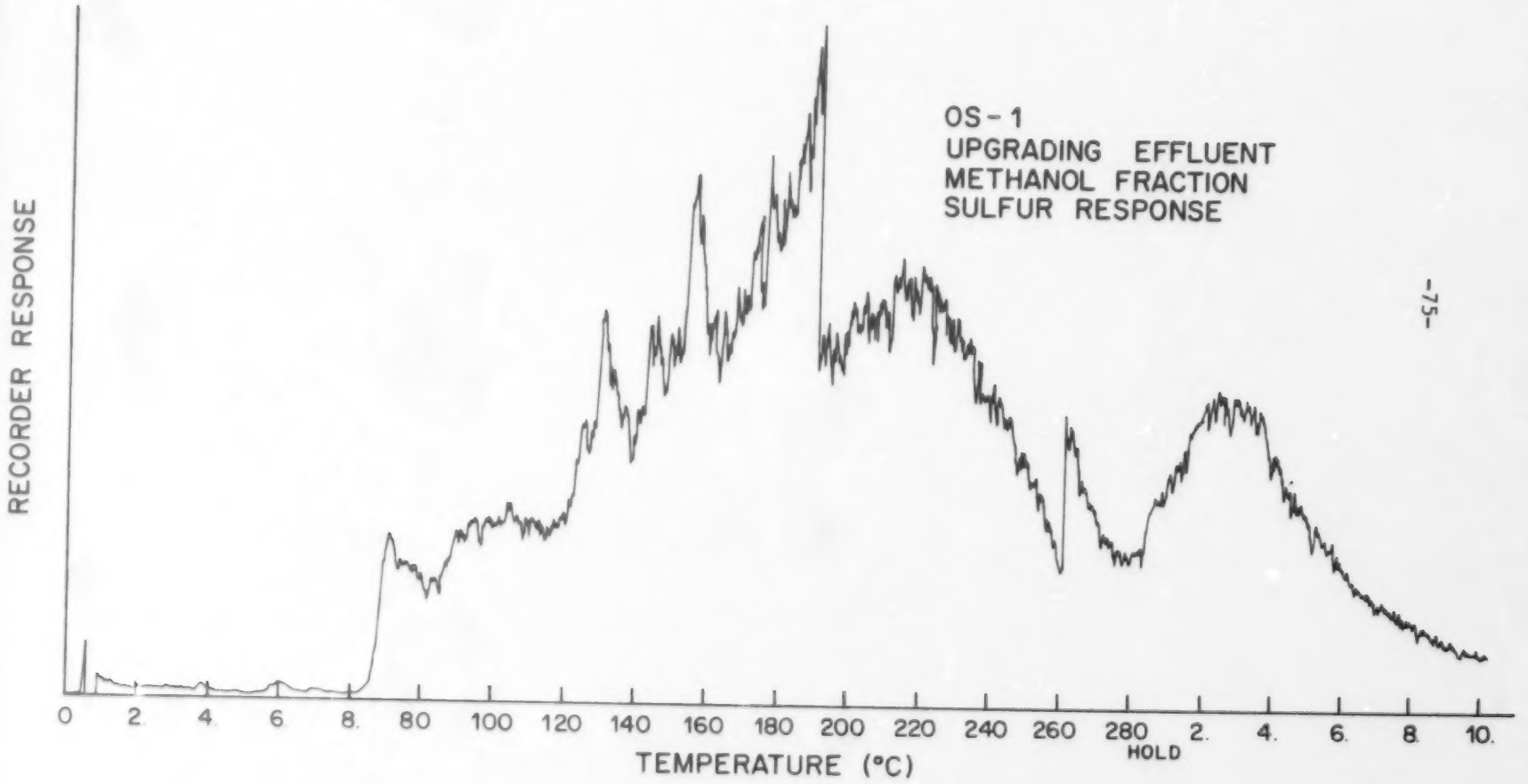
OS-1
UPGRADING EFFLUENT
METHANOL FRACTION
SULFUR RESPONSE
RECORDER RESPONSE
0 2. 4. 6. 8. 80 100 120 140 160 180 200 220 240 260 280 2. 4. 6. 8. 10.
HOLD
TEMPERATURE (°C)

Figure 30

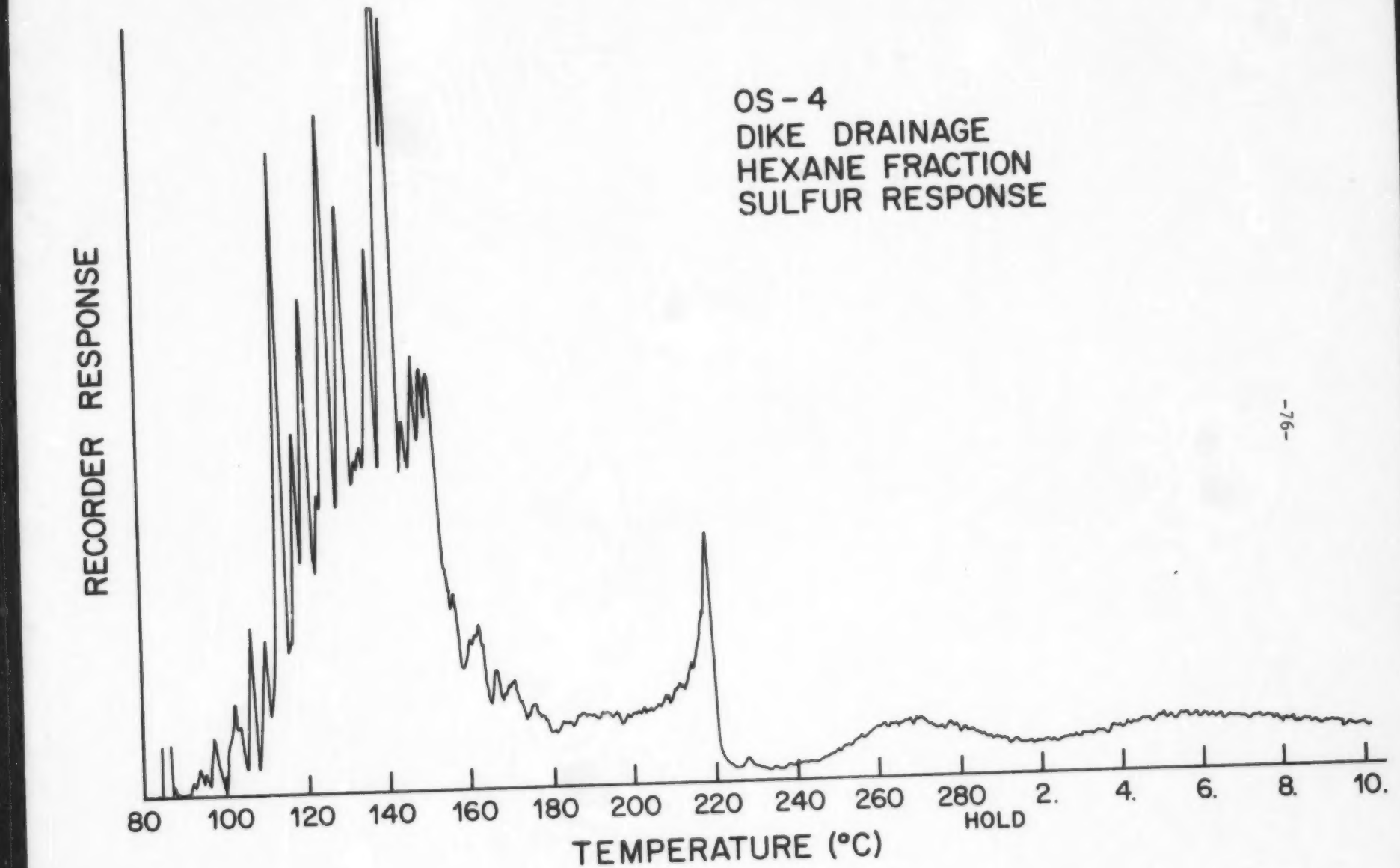
OS-4
DIKE DRAINAGE
HEXANE FRACTION
SULFUR RESPONSE
RECORDER RESPONSE
80
100
120
140
160
180
200
220
240
260
280
HOLD
2.
4.
6.
8.
10.
TEMPERATURE (°C)

Figure 31

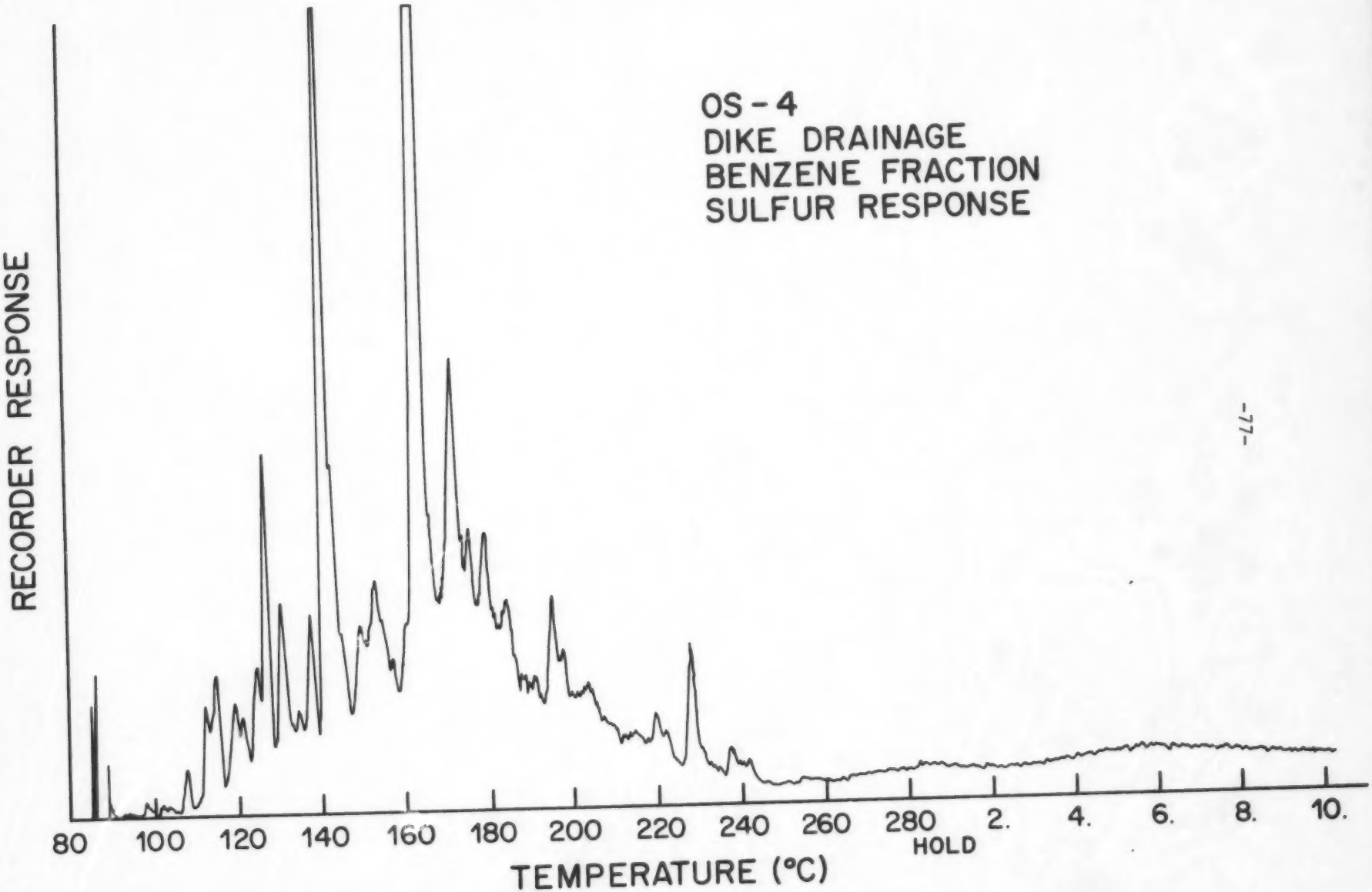
OS - 4
DIKE DRAINAGE
BENZENE FRACTION
SULFUR RESPONSE
RECORDER RESPONSE
80
100
120
140
160
180
200
220
240
260
280
2.
4.
6.
8.
10.
HOLD
TEMPERATURE (°C)

Figure 32

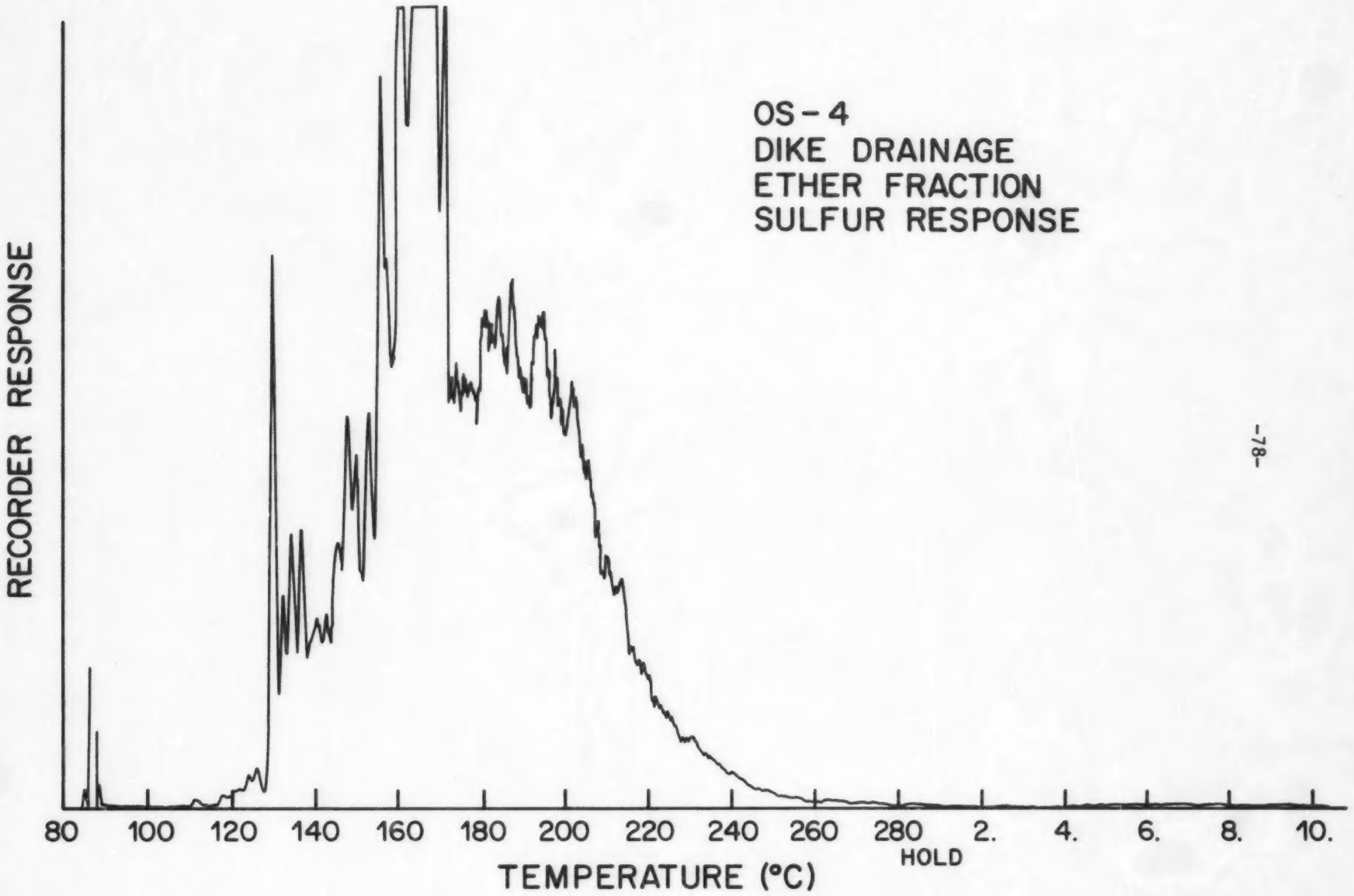
OS-4
DIKE DRAINAGE
ETHER FRACTION
SULFUR RESPONSE
RECORDER RESPONSE
80
100
120
140
160
180
200
220
240
260
280
2.
4.
6.
8.
10.
HOLD
TEMPERATURE (°C)

Figure 33

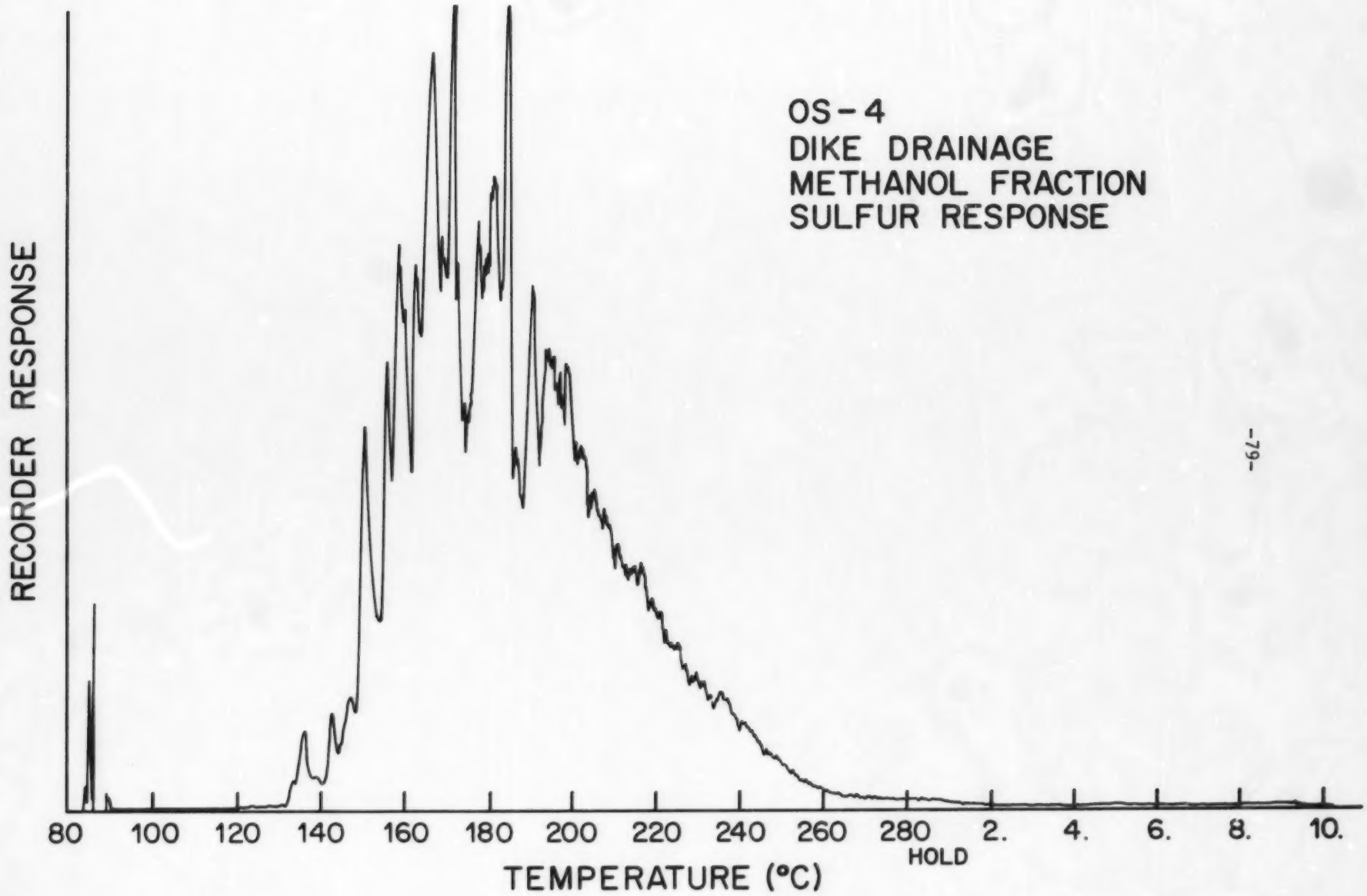
OS-4
DIKE DRAINAGE
METHANOL FRACTION
SULFUR RESPONSE
RECORDER RESPONSE
80
100
120
140
160
180
200
220
240
260
280
2.
4.
6.
8.
10.
HOLD
TEMPERATURE (°C)

Figure 34

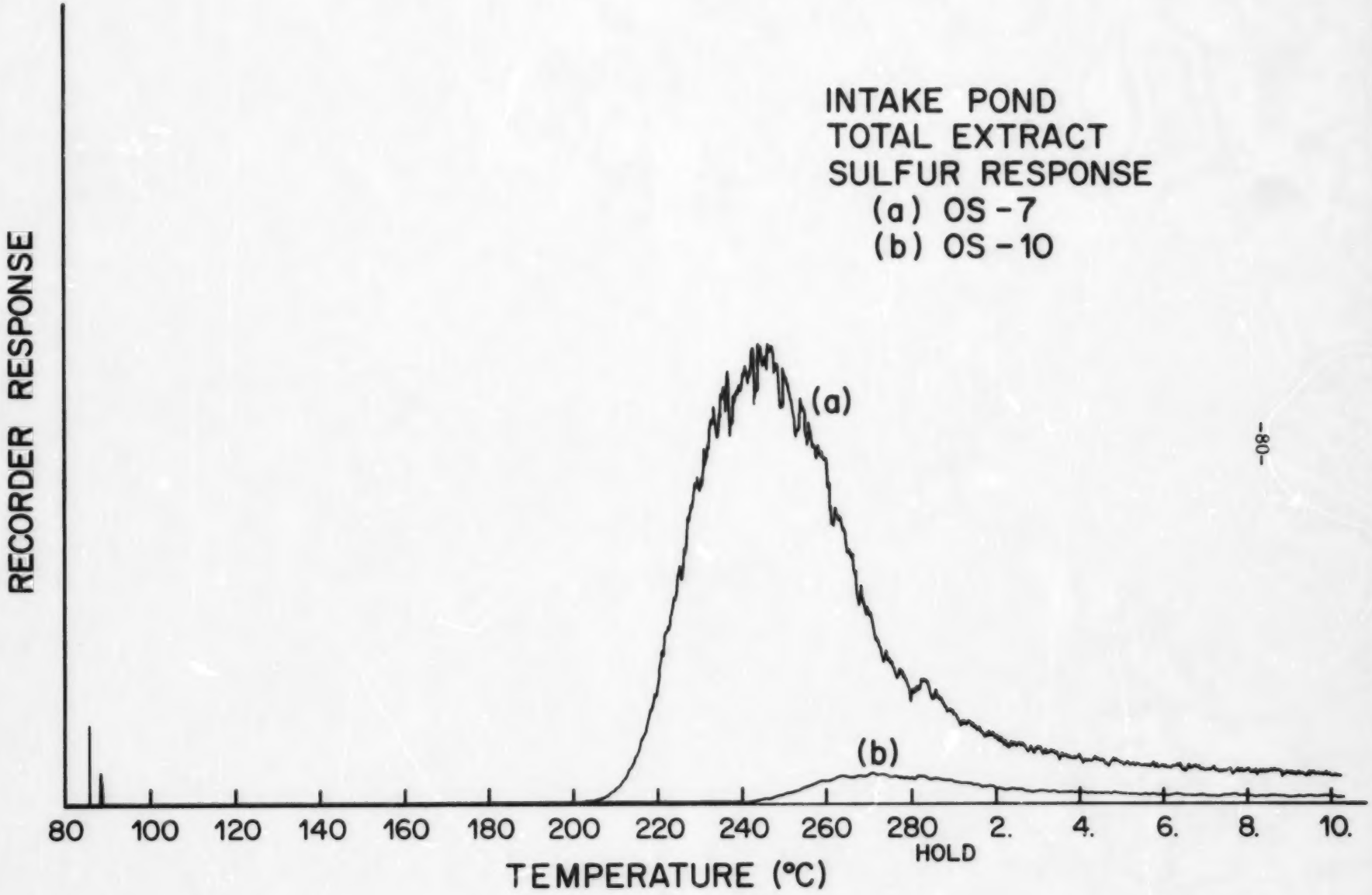
INTAKE POND
TOTAL EXTRACT
SULFUR RESPONSE
(a) OS-7
(b) OS-10
RECORDER RESPONSE
(a)
(b)
80 100 120 140 160 180 200 220 240 260 280 2. 4. 6. 8. 10.
HOLD
TEMPERATURE (°C)

Figure 35

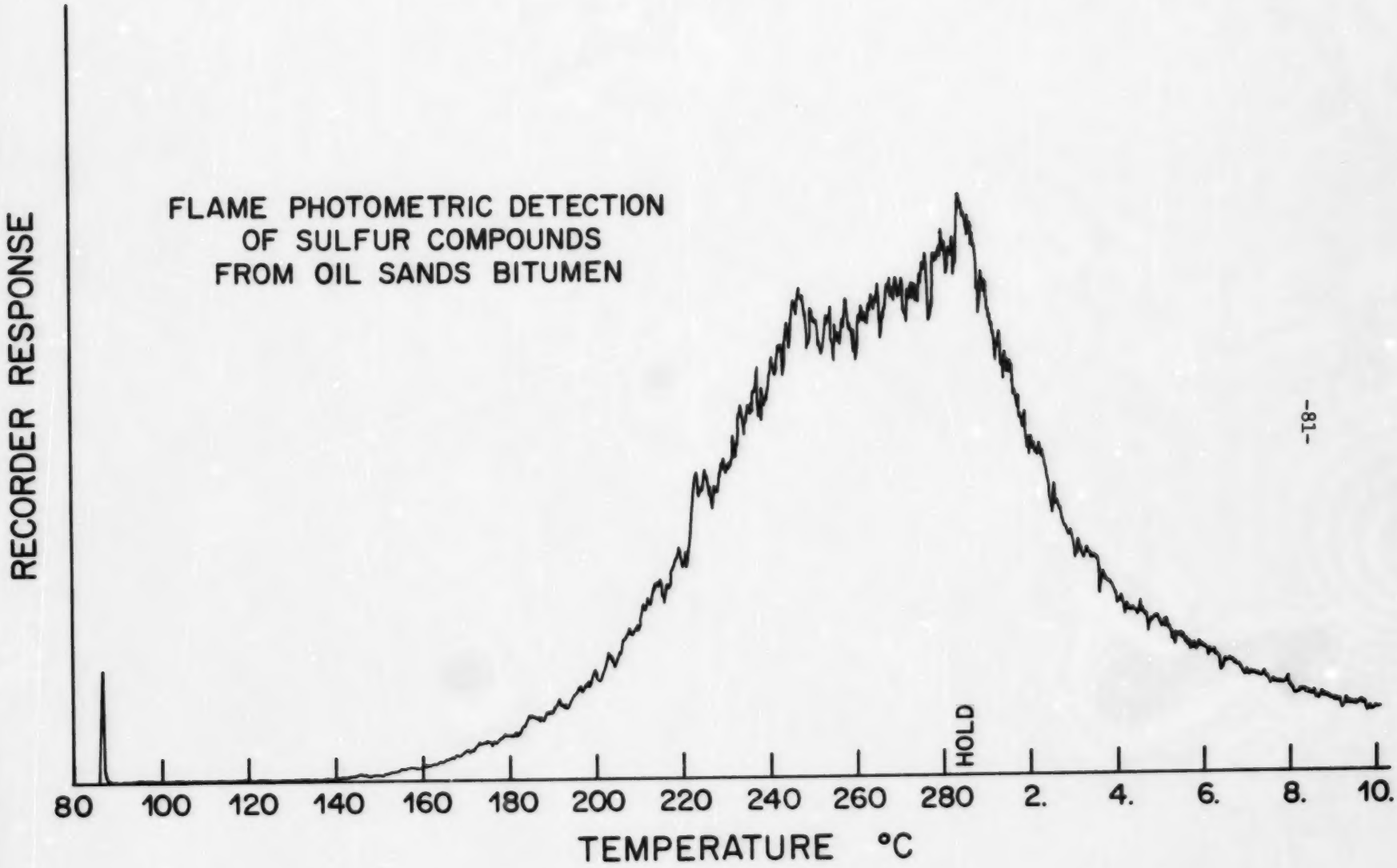
FLAME PHOTOMETRIC DETECTION
OF SULFUR COMPOUNDS
FROM OIL SANDS BITUMEN
RECORDER RESPONSE
HOLD
80
100
120
140
160
180
200
220
240
260
280
2.
4.
6.
8.
10.
TEMPERATURE °C

Figure 36

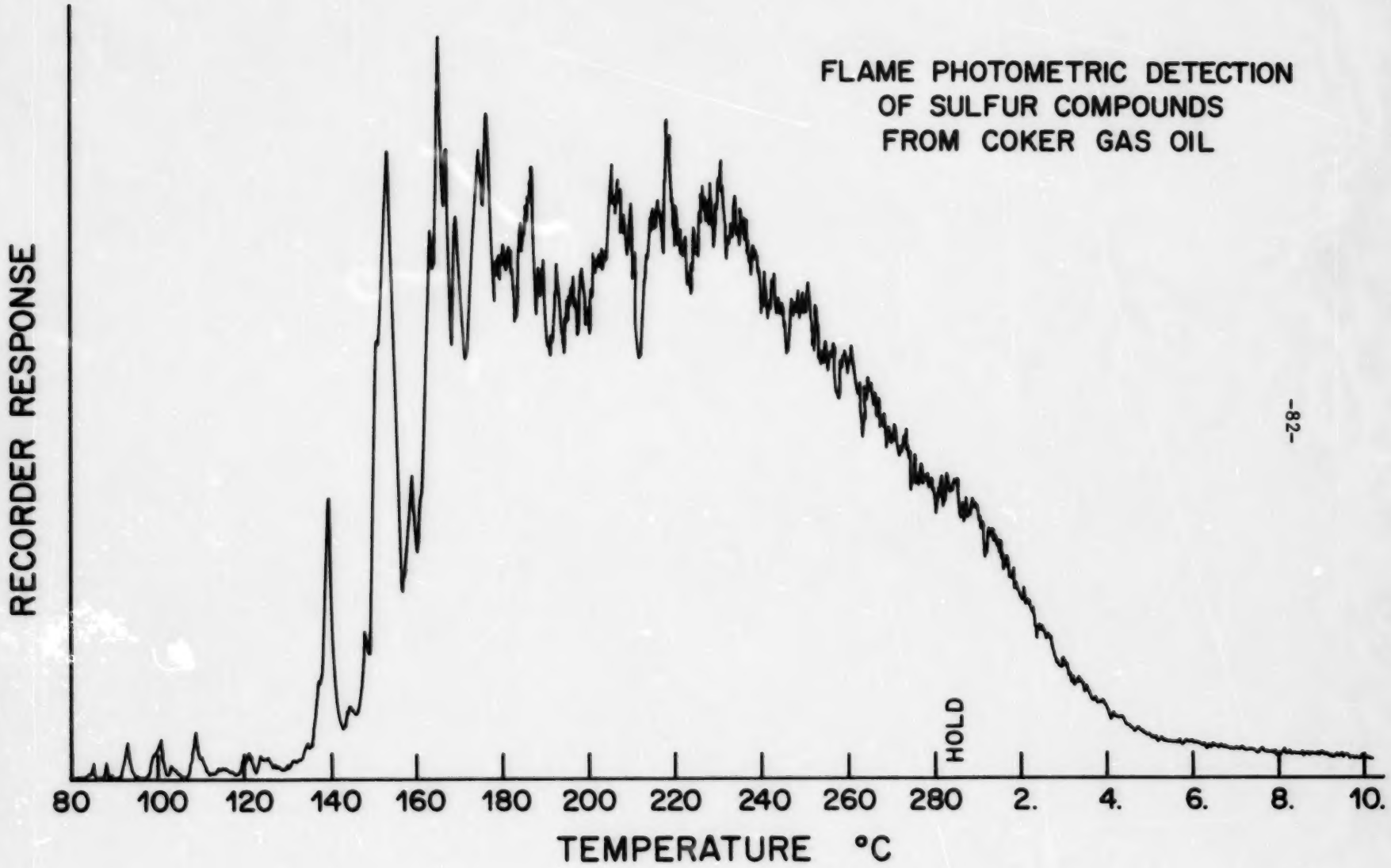
FLAME PHOTOMETRIC DETECTION
OF SULFUR COMPOUNDS
FROM COKER GAS OIL
RECORDER RESPONSE
HOLD
80 100 120 140 160 180 200 220 240 260 280 2. 4. 6. 8. 10.
TEMPERATURE °C

Figure 37

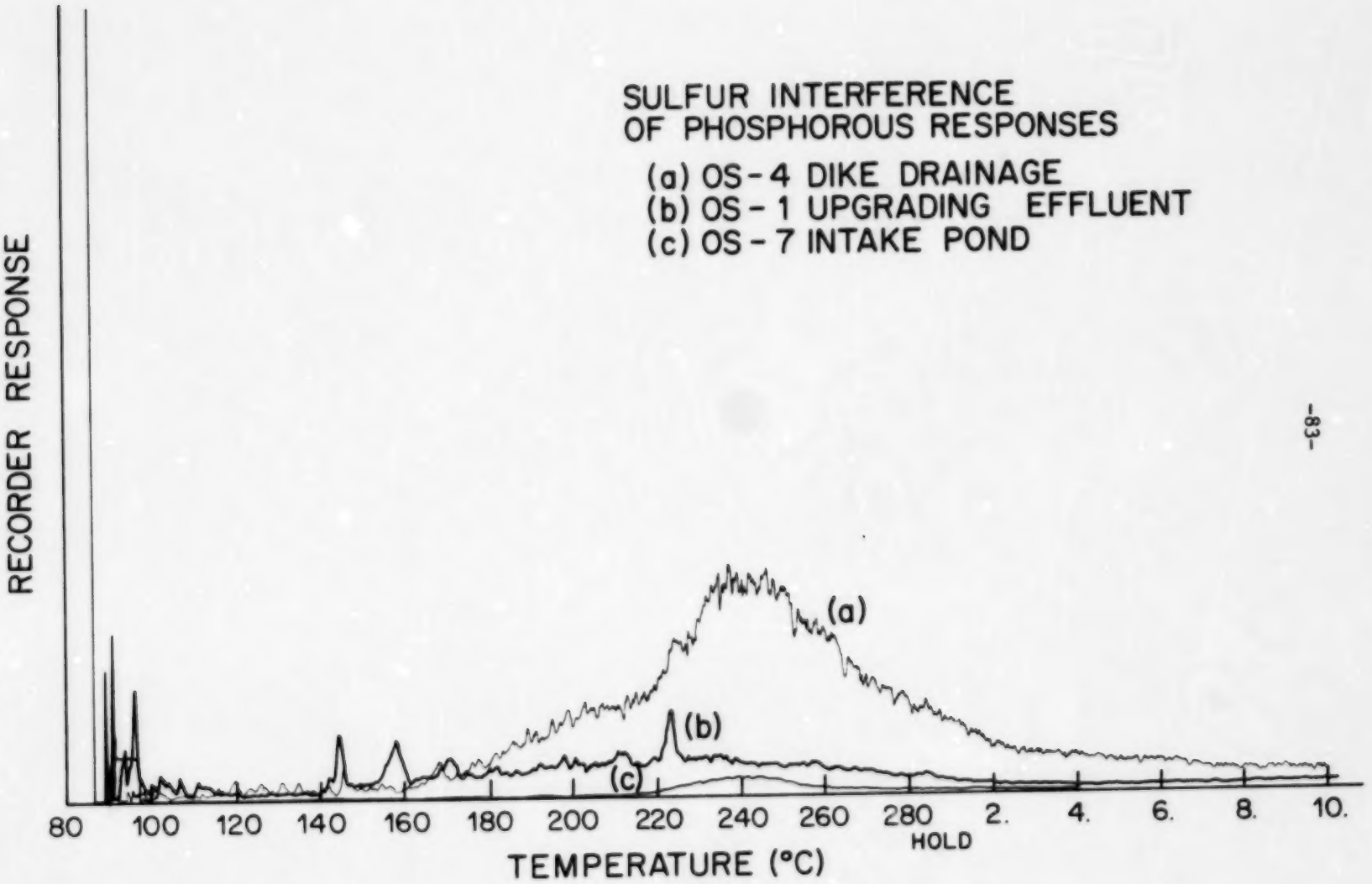
SULFUR INTERFERENCE
OF PHOSPHOROUS RESPONSES
(a) OS-4 DIKE DRAINAGE
(b) OS-1 UPGRADING EFFLUENT
(c) OS-7 INTAKE POND
RECORDER RESPONSE
(a)
(b)
(c)
80
100
120
140
160
180
200
220
240
260
280
2.
4.
6.
8.
10.
HOLD
TEMPERATURE (°C)

Figure 38

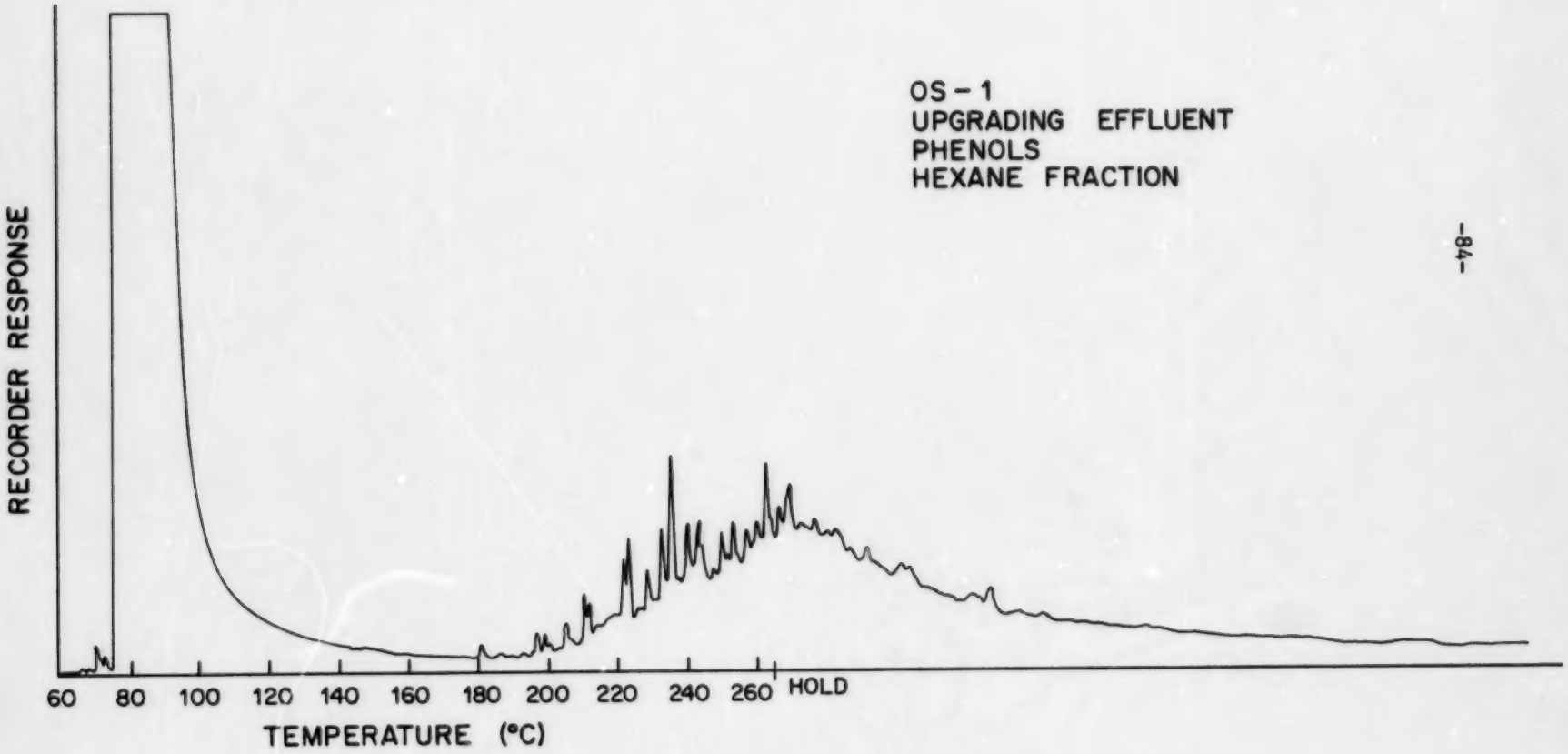
OS - 1
UPGRADING EFFLUENT
PHENOLS
HEXANE FRACTION
RECORDER RESPONSE
60
80
100
120
140
160
180
200
220
240
260
HOLD
TEMPERATURE (°C)

Figure 39

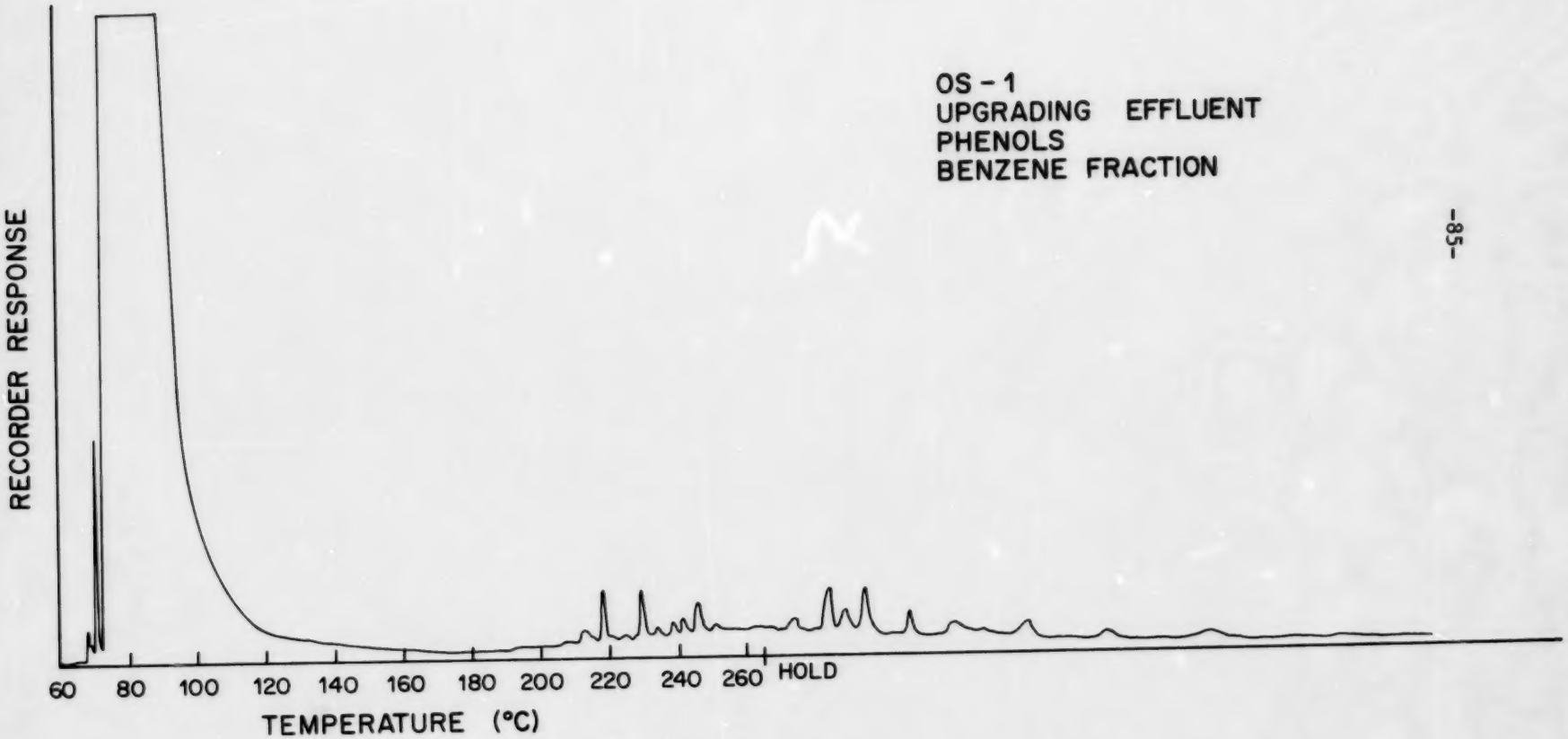
OS - 1
UPGRADING EFFLUENT
PHENOLS
BENZENE FRACTION
RECORDER RESPONSE
60
80
100
120
140
160
180
200
220
240
260
HOLD
TEMPERATURE (°C)

Figure 40

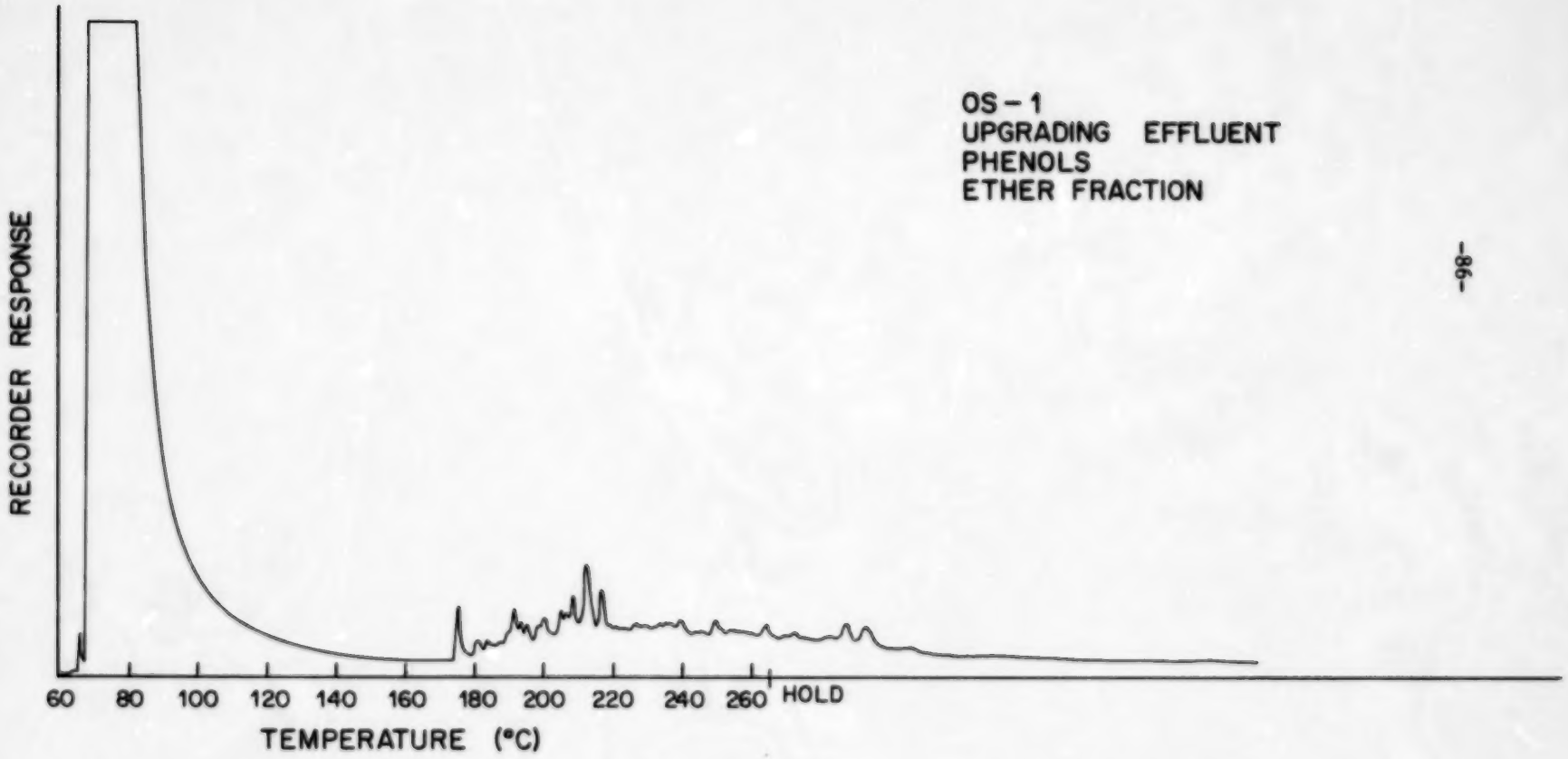
OS – 1
UPGRADING EFFLUENT
PHENOLS
ETHER FRACTION
RECORDER RESPONSE
60
80
100
120
140
160
180
200
220
240
260
HOLD
TEMPERATURE (°C)

Figure 41

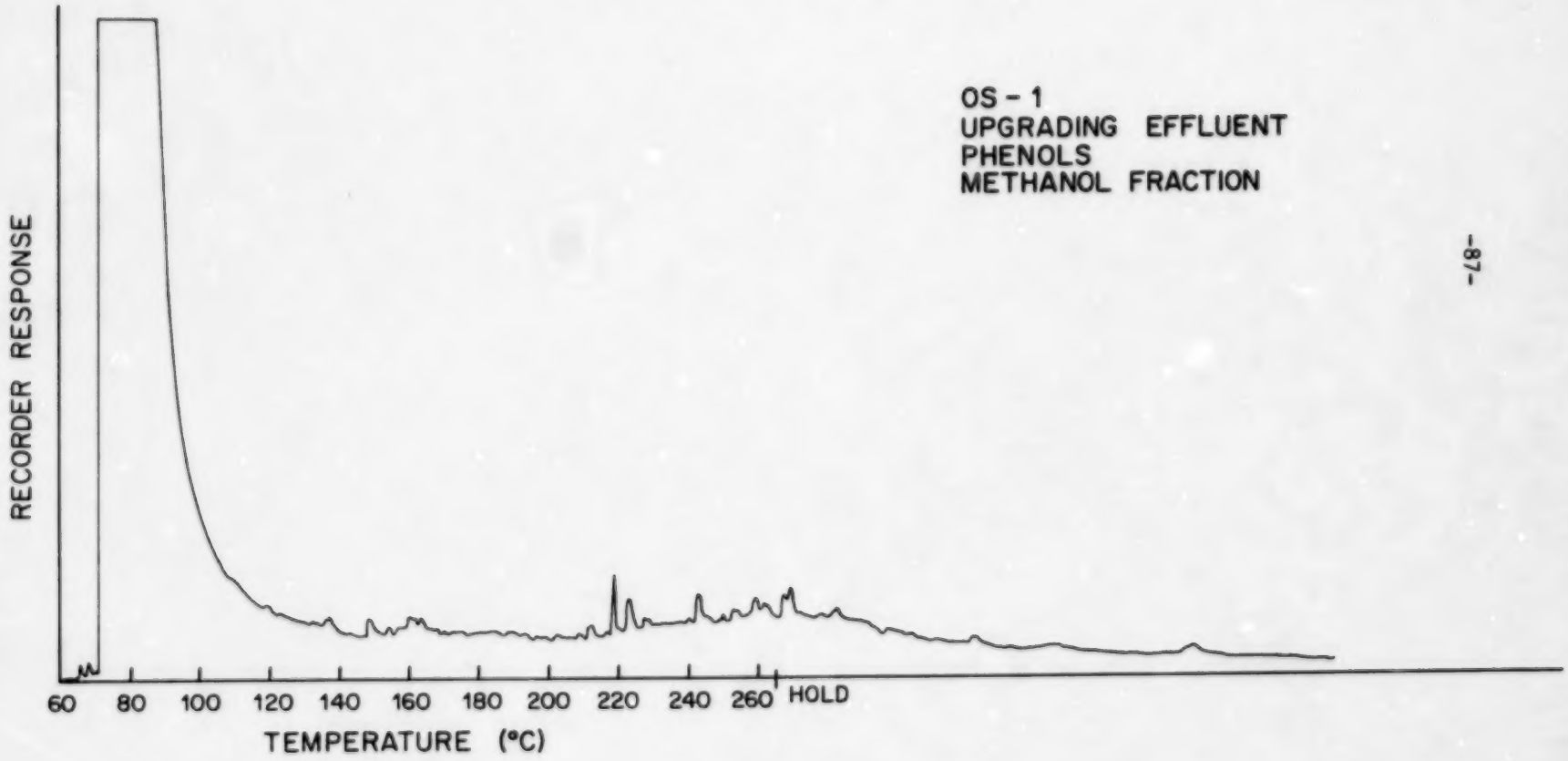
OS - 1
UPGRADING EFFLUENT
PHENOLS
METHANOL FRACTION
RECORDER RESPONSE
60
80
100
120
140
160
180
200
220
240
260
HOLD
TEMPERATURE (°C)

Figure 42

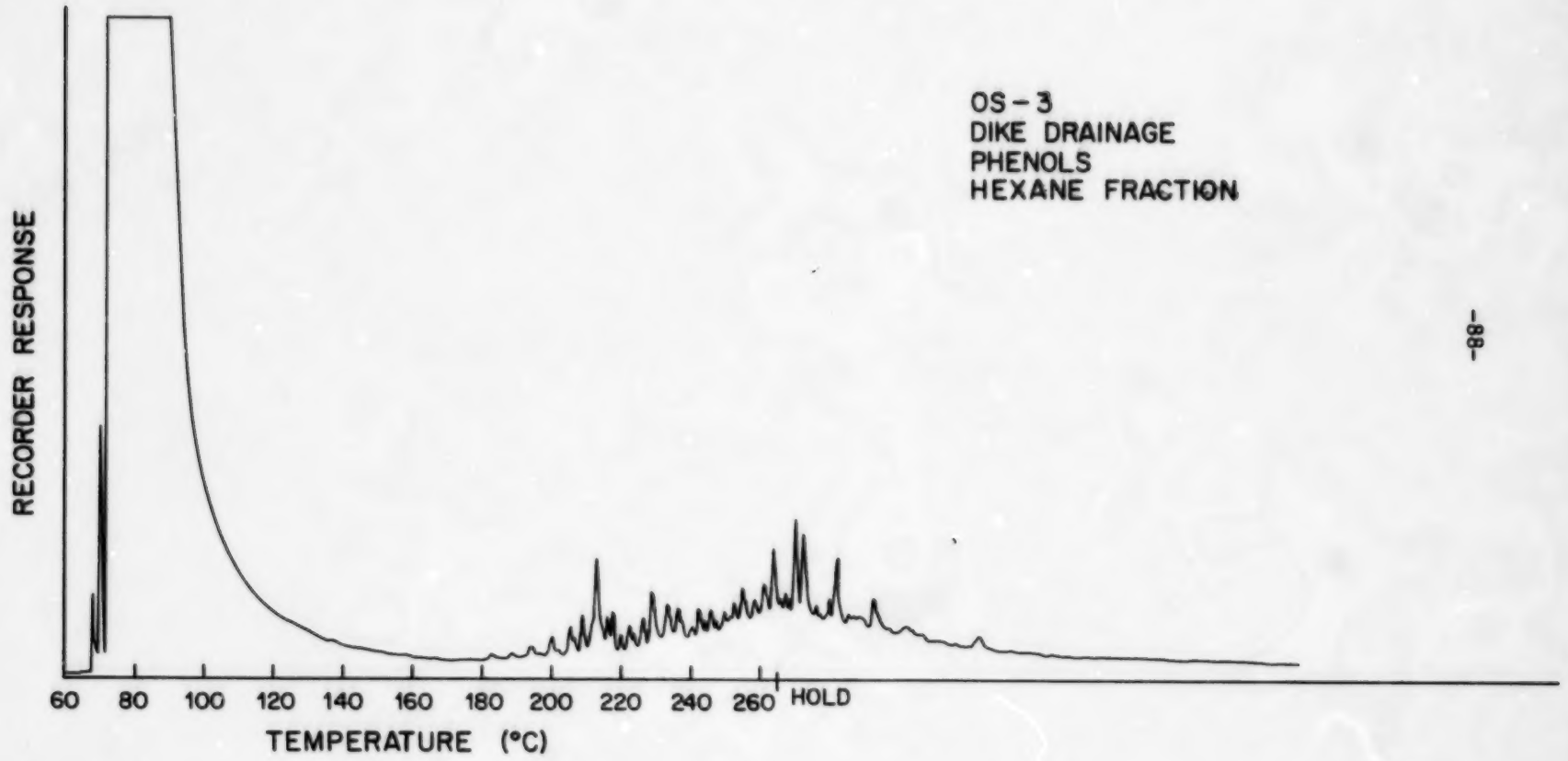
OS-3
DIKE DRAINAGE
PHENOLS
HEXANE FRACTION
RECORDER RESPONSE
60
80
100
120
140
160
180
200
220
240
260
HOLD
TEMPERATURE (°C)

Figure 43

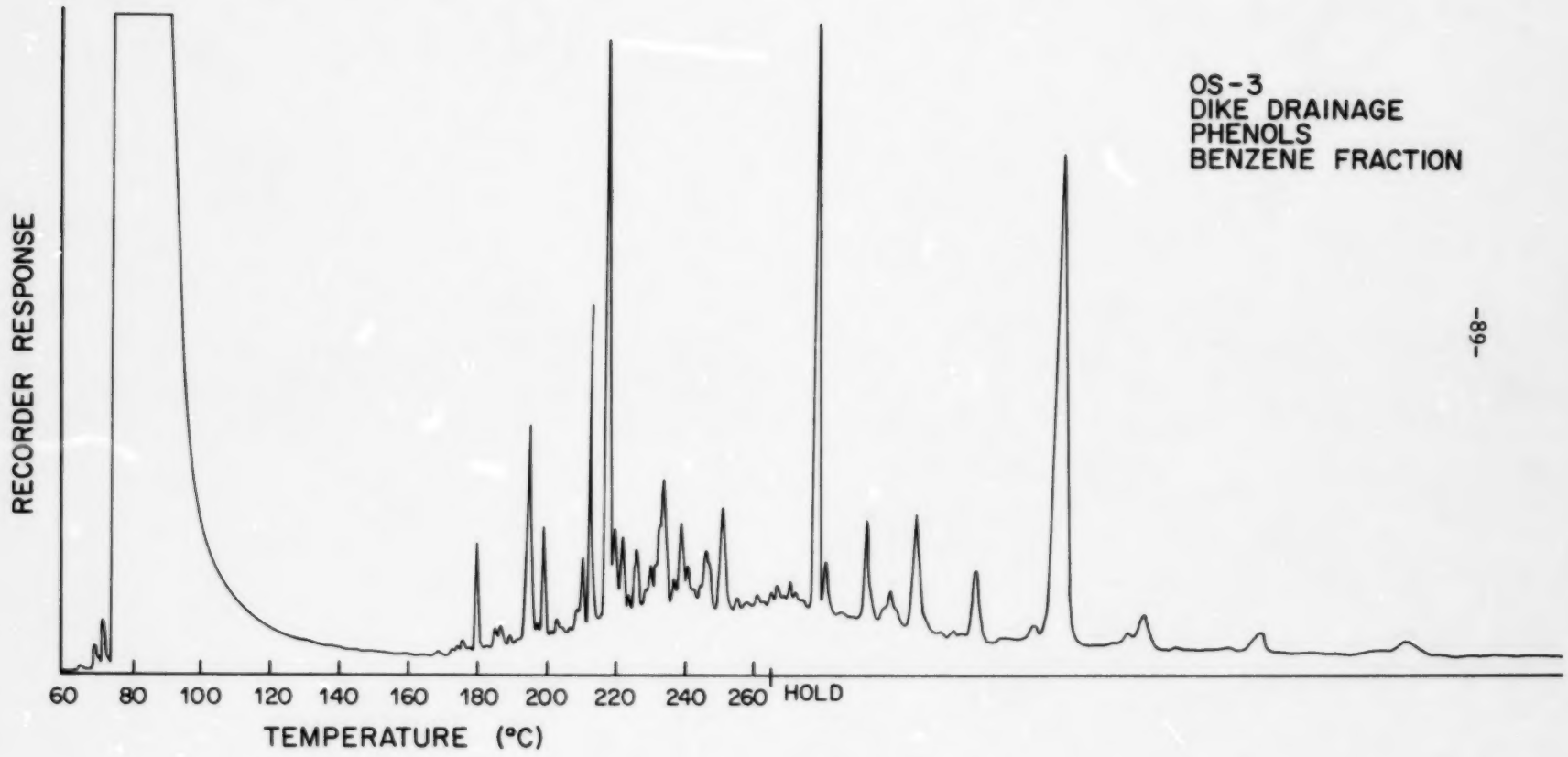
OS-3
DIKE DRAINAGE
PHENOLS
BENZENE FRACTION
RECORDER RESPONSE
60 80 100 120 140 160 180 200 220 240 260 HOLD
TEMPERATURE (°C)

Figure 44

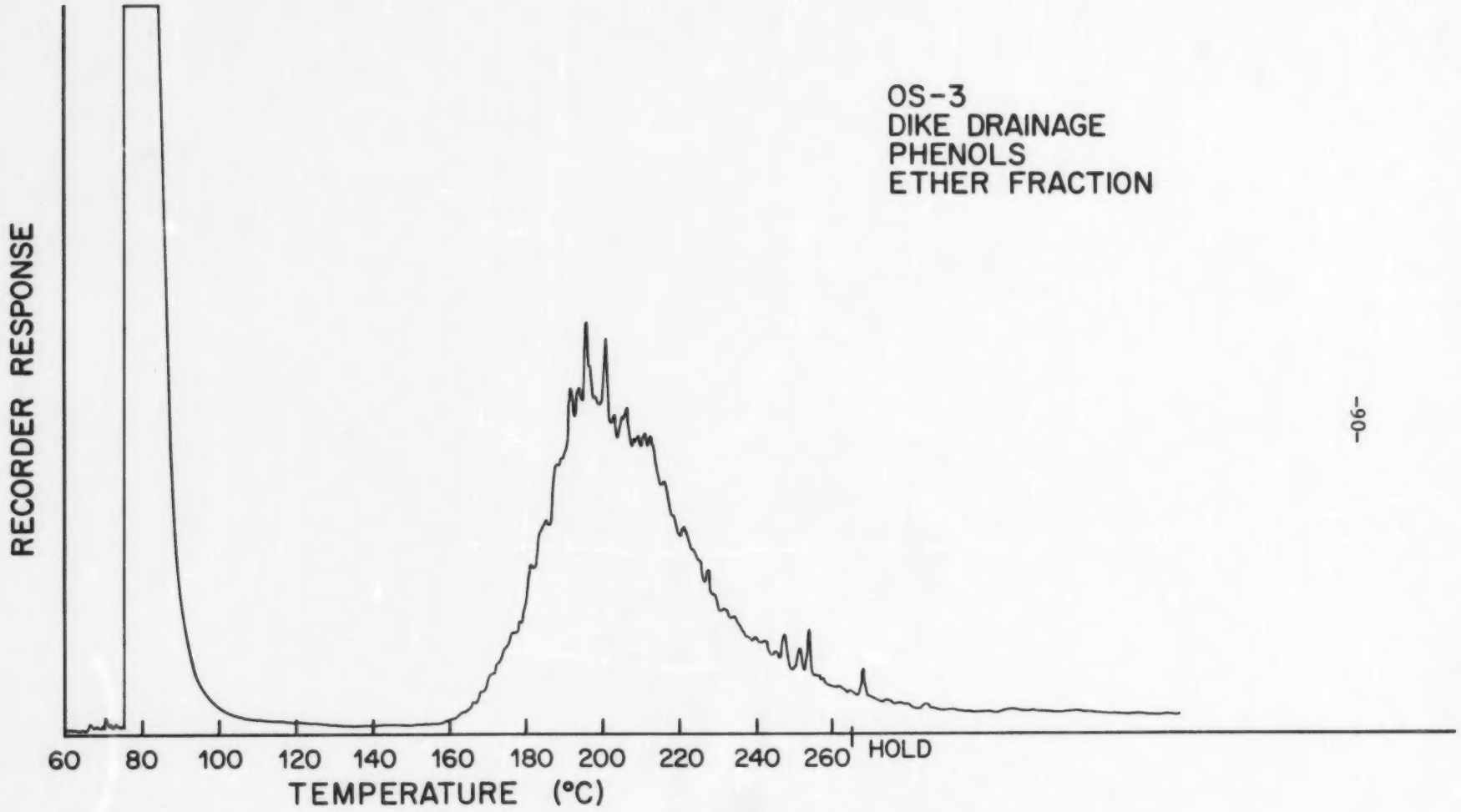
OS-3
DIKE DRAINAGE
PHENOLS
ETHER FRACTION
RECORDER RESPONSE
60
80
100
120
140
160
180
200
220
240
260
HOLD
TEMPERATURE (°C)

Figure 45

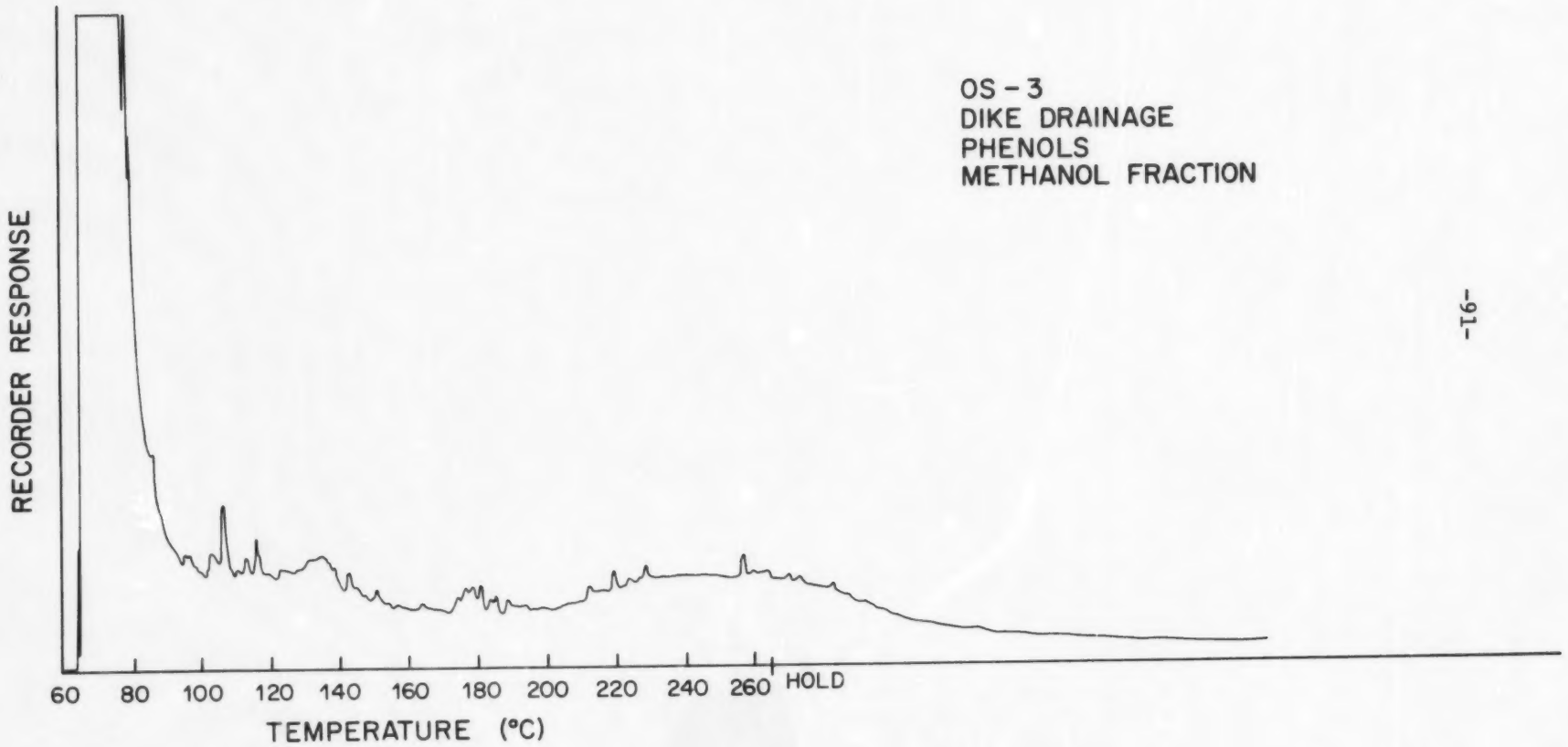
OS - 3
DIKE DRAINAGE
PHENOLS
METHANOL FRACTION
RECORDER RESPONSE
60
80
100
120
140
160
180
200
220
240
260
HOLD
TEMPERATURE (°C)

Figure 46

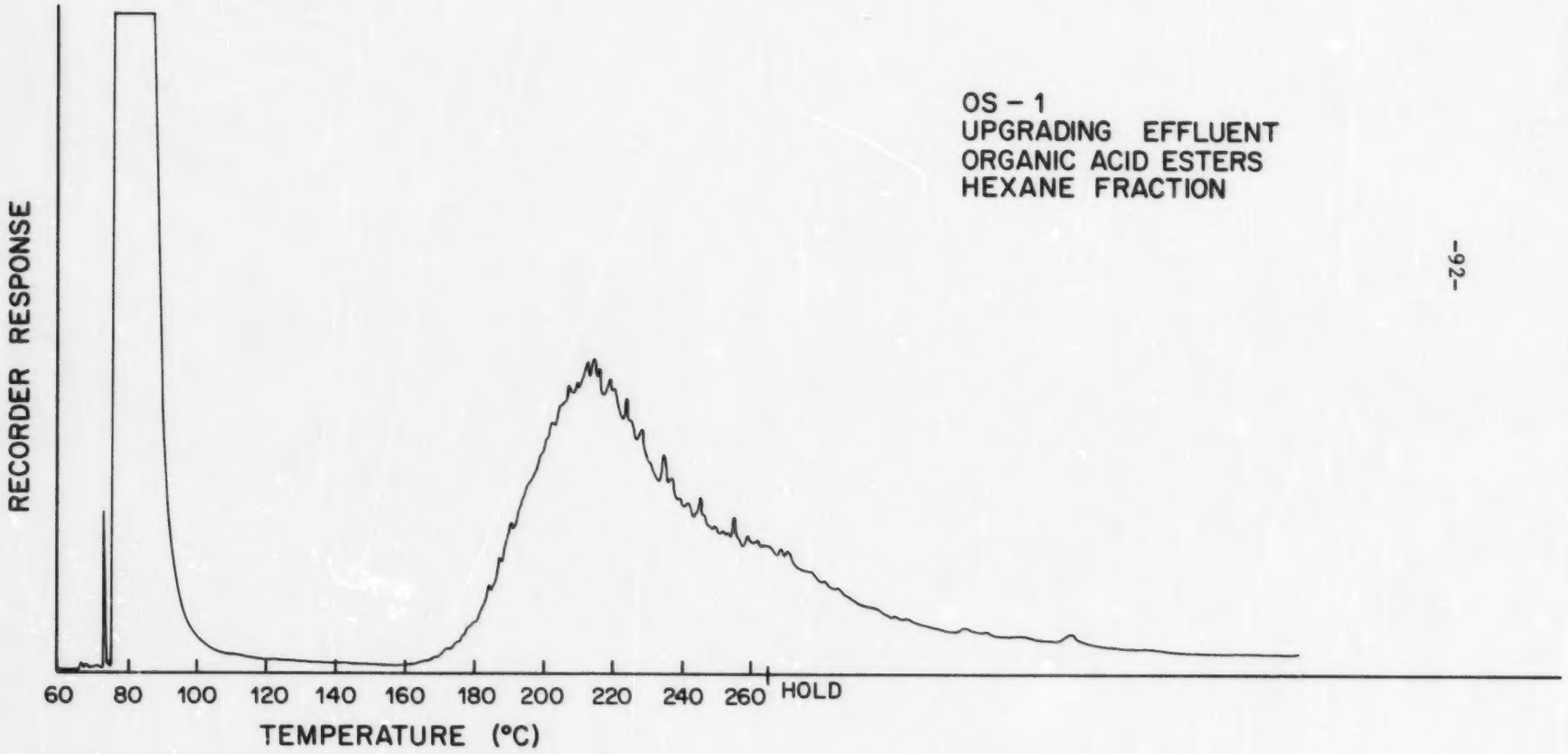
OS – 1
UPGRADING EFFLUENT
ORGANIC ACID ESTERS
HEXANE FRACTION
RECORDER RESPONSE
60 80 100 120 140 160 180 200 220 240 260 HOLD
TEMPERATURE (°C)

Figure 47

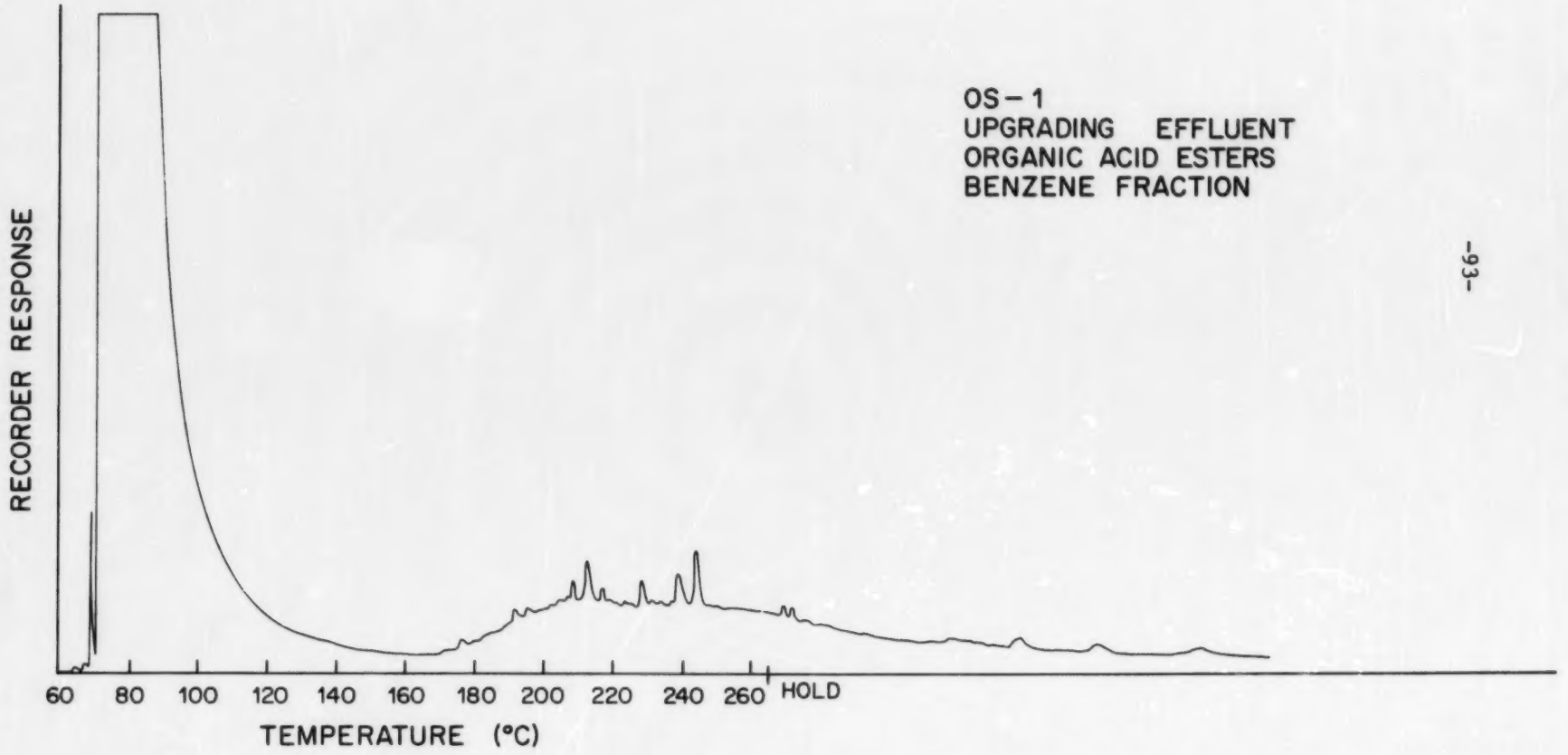
OS – 1
UPGRADING EFFLUENT
ORGANIC ACID ESTERS
BENZENE FRACTION
RECORDER RESPONSE
60 80 100 120 140 160 180 200 220 240 260 HOLD
TEMPERATURE (°C)

Figure 48

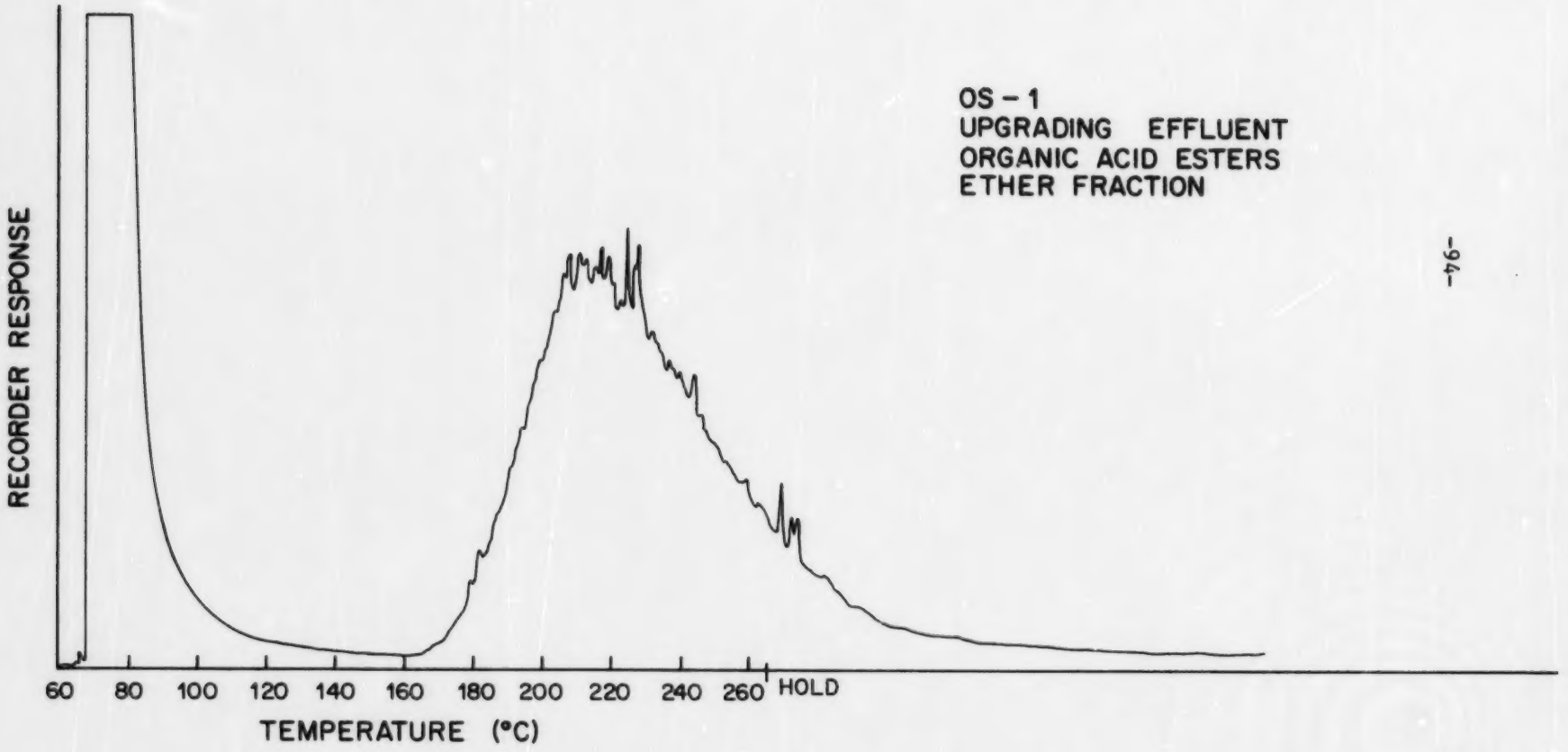
OS - 1
UPGRADING EFFLUENT
ORGANIC ACID ESTERS
ETHER FRACTION
RECORDER RESPONSE
60 80 100 120 140 160 180 200 220 240 260 HOLD
TEMPERATURE (°C)

Figure 49

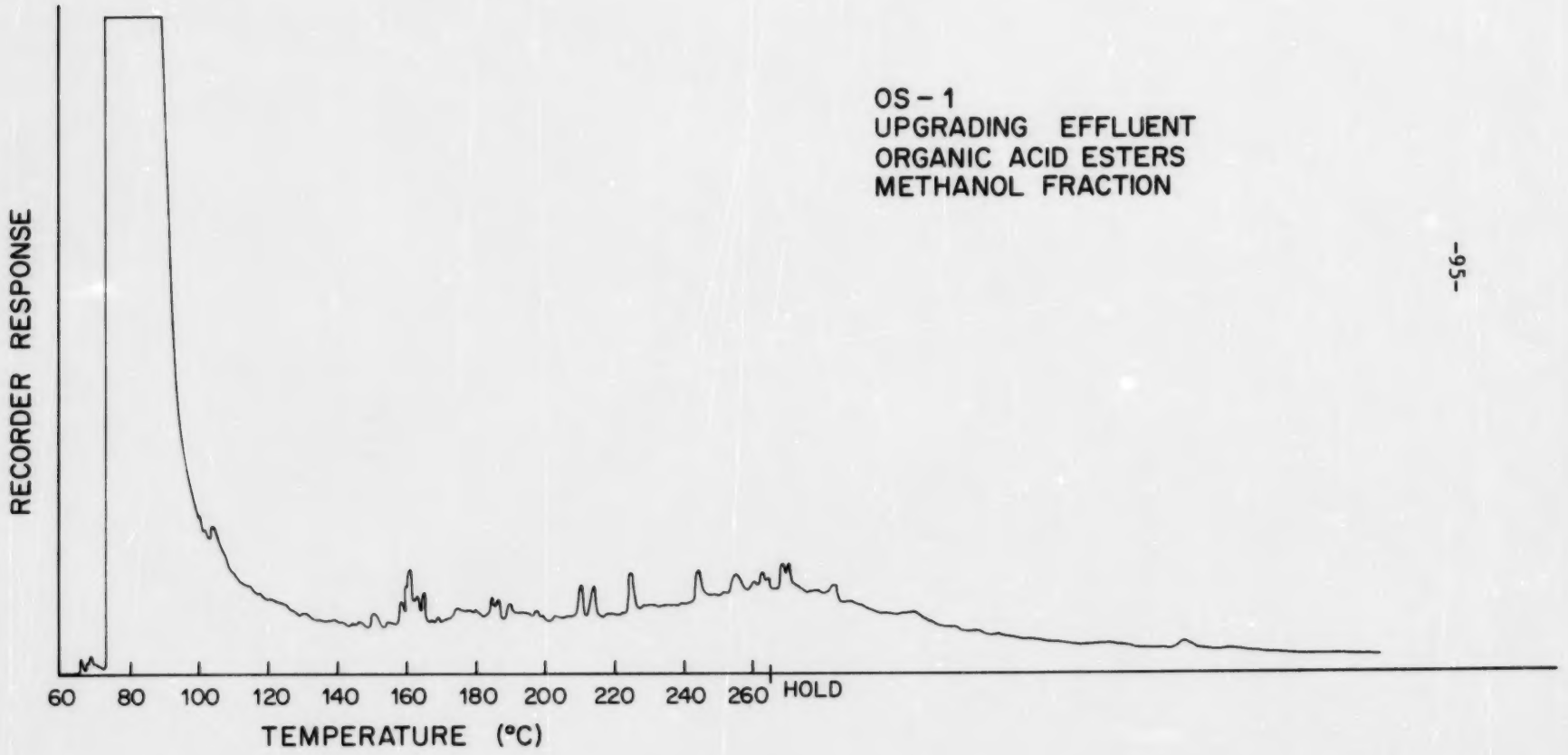
OS – 1
UPGRADING EFFLUENT
ORGANIC ACID ESTERS
METHANOL FRACTION
RECORDER RESPONSE
60
80
100
120
140
160
180
200
220
240
260
HOLD
TEMPERATURE (°C)

Figure 50

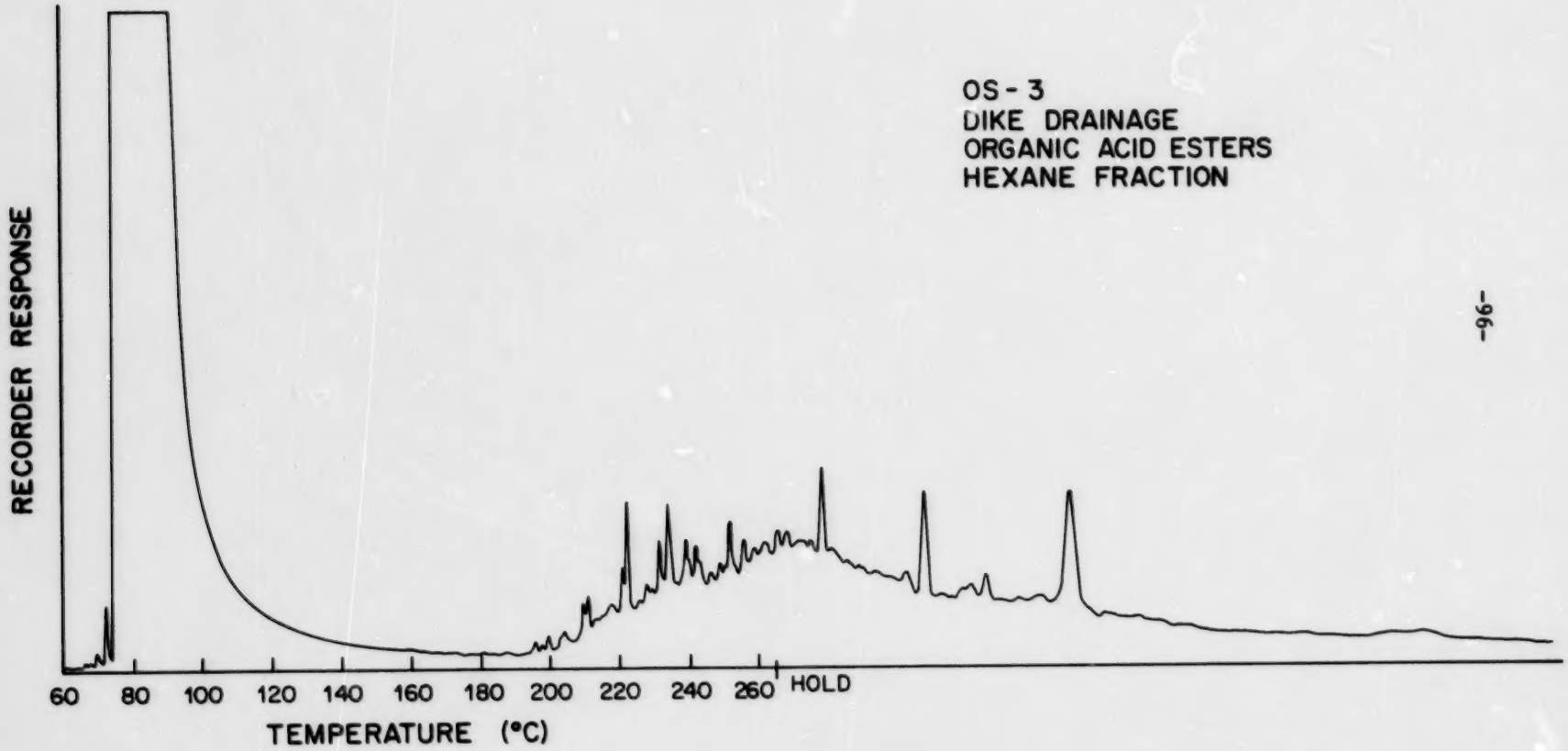
OS - 3
DIKE DRAINAGE
ORGANIC ACID ESTERS
HEXANE FRACTION
RECORDER RESPONSE
60
80
100
120
140
160
180
200
220
240
260
HOLD
TEMPERATURE (°C)

Figure 51

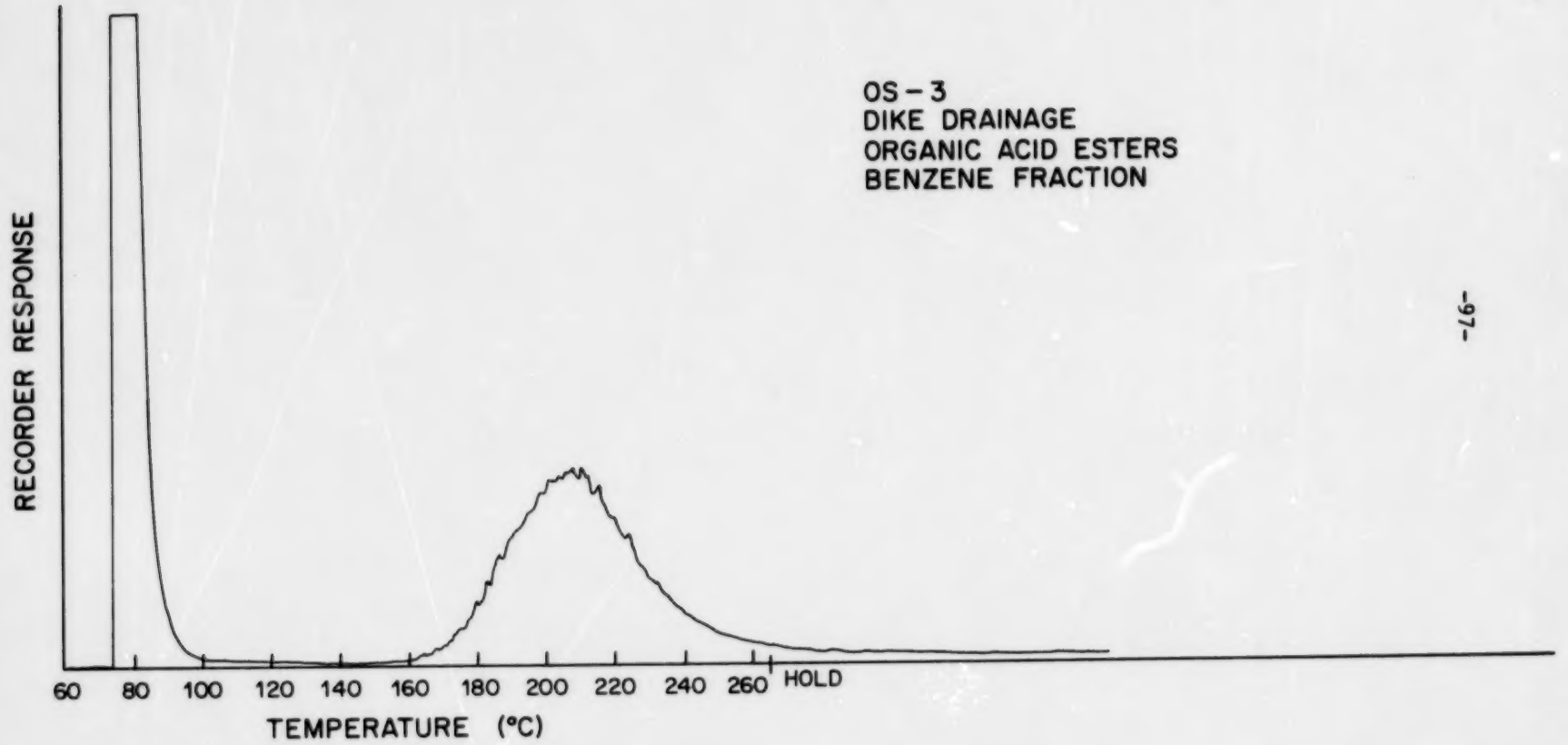
OS – 3
DIKE DRAINAGE
ORGANIC ACID ESTERS
BENZENE FRACTION
RECORDER RESPONSE
60
80
100
120
140
160
180
200
220
240
260
HOLD
TEMPERATURE (°C)

Figure 52

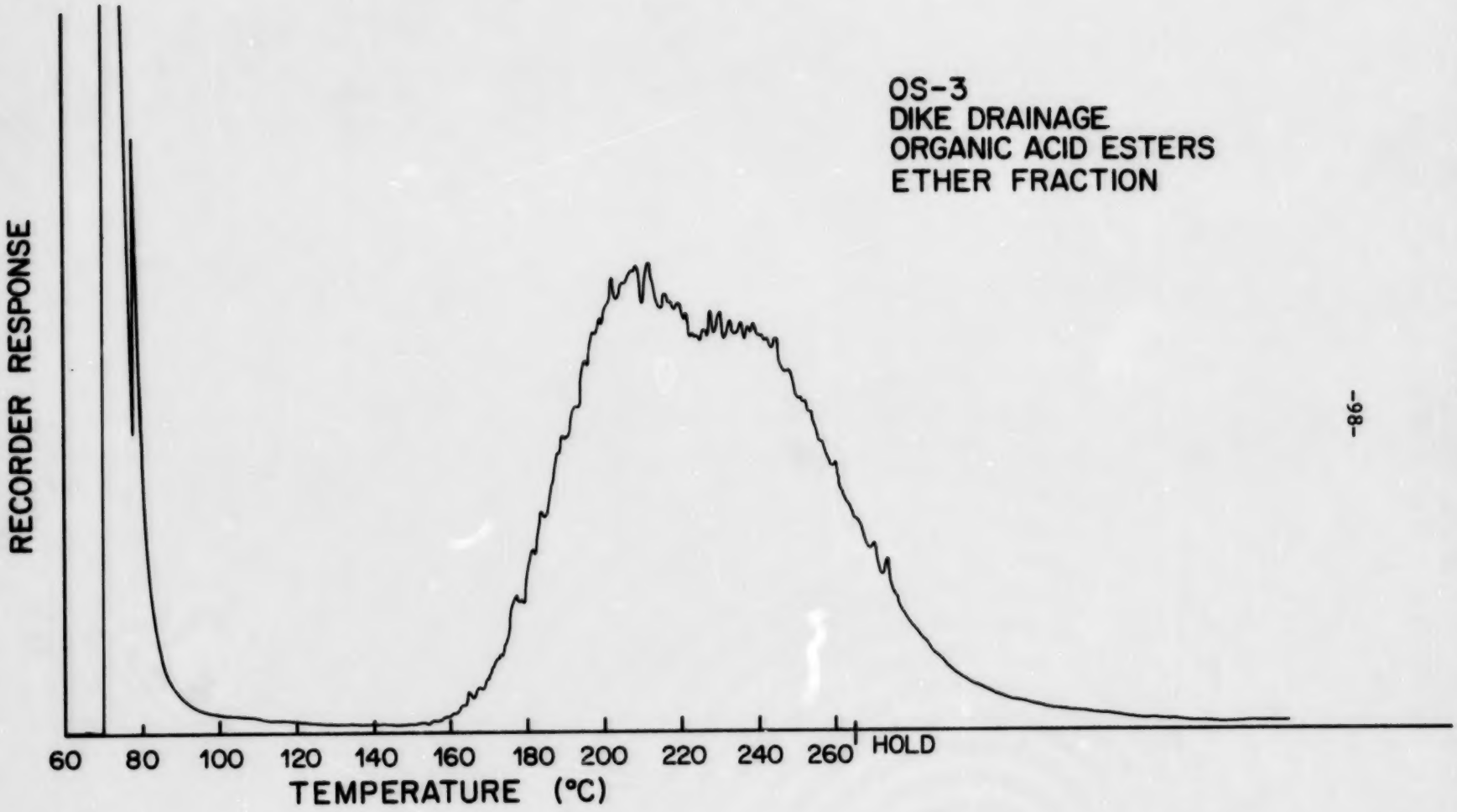
OS-3
DIKE DRAINAGE
ORGANIC ACID ESTERS
ETHER FRACTION
RECORDER RESPONSE
60
80
100
120
140
160
180
200
220
240
260
HOLD
TEMPERATURE (°C)

Figure 53

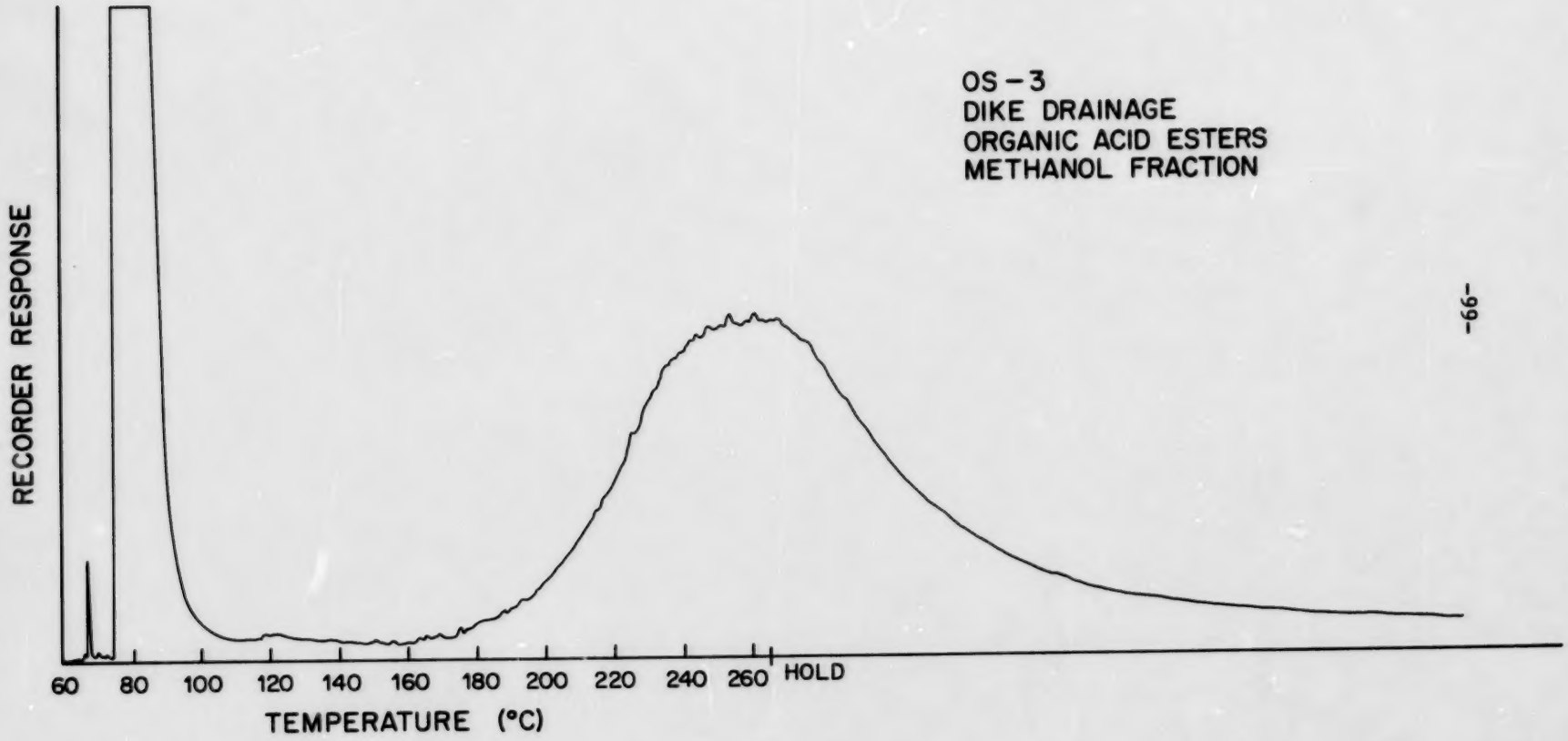
OS – 3
DIKE DRAINAGE
ORGANIC ACID ESTERS
METHANOL FRACTION
RECORDER RESPONSE
60
80
100
120
140
160
180
200
220
240
260
HOLD
TEMPERATURE (°C)

Figure 54

8. APPENDIX--TERMS OF REFERENCE

Evaluation of Oilsands Extraction Plant Tailings Pond Wastewater

Supply and Services Canada Contract No. SS02-KE204-5-EP32

REQUIREMENT:

A. Objectives:

This phase of the study program is to:

1. Characterize and quantify into compound classes the total organic component of wastewaters from an existing oilsands extracting plant including the seepage from the tailings pond and wastewaters potentially disposable to the tailings pond such as bitumen upgrading effluent and coke storage area runoff.

2. Specifically identify all organic compounds detected within component classifications, where identification is possible and the specific identity of the compound would possibly qualify it as an environmental contaminant.

3. Characterize and quantify the presence of specific heavy metal components of the wastewaters specified in (1).

B. Statement of Work:

The study and preparation of the report will require the following:

1. Provide clear and concise instructions and contaminant free containers for the collection of wastewater samples. Sample collection is not a part of the requirement.

2. Analyse up to ten samples for total organic carbon to quantify the organic component.

3. Extract the organic component from up to ten wastewater samples and using suitable separation techniques such as column and/or thin layer chromatography separate the total organic component and proceed by available analytical techniques to characterize and quantify the organic component into a compound classification scheme. For example:
   - (a) alkanes and alkenes (unsubstituted)
   - (b) alkanes and alkenes (halogenated)
   - (c) alcohols
   - (d) amines (aliphatic and aromatic)
   - (e) nitriles
   - (f) heterocyclics (nitrogen, oxygen or sulphur)
   - (g) organic acids (carboxylic, sulphonic)
   - (h) carboxylic esters (i.e., phthalate acid esters)
   - (i) amides (i.e., carbamates, thio carbamates)
   - (j) phosphate esters
   - (k) aldehydes, ketones and esters

(l) aromatics (unsubstituted)
(m) aromatic derivatives
(n) phenols and quinones
(o) organic sulphur compounds (i.e., mercaptans)
(p) organometallic compounds

This breakdown is idealistic and may require modification.

4. Utilizing gas chromatography, mass spectrometry, computerized mass spectra facilities and other applicable organic analytical techniques identify all clearly separable and identifiable organic compounds in those groups of compounds which may contain environmental contaminants.

5. Consult regularly (at least monthly) with Oil Sands Environmental Research Program staff in the Environmental Protection Service to review progress and seek guidance on the significance of identified organic compounds.

6. Scan up to 10 wastewater samples for the semiquantitative determination of heavy metal constituents by means of emission spectroscopy, x-ray fluorescence or other suitable analytical techniques.

7. Analyse the 10 wastewater samples specifically for the concentration of total vanadium.

PROPOSED PERIOD OF CONTRACT: September 8, 1975 to March 31, 1976.

SCIENTIFIC AUTHORITY:

Water Pollution Control Directorate
Northwest Region
Environmental Protection Service
Environment Canada
Edmonton, Alberta.

The Scientific Authority will be responsible for all matters concerning the scientific and technological content of the work requirements.

SCIENCE PROCUREMENT MANAGER:

Mr. John R. Holinsky
Science Procurement Branch
Supply and Services Canada
Metcalfe Building, 9th floor
88 Metcalfe Street
Ottawa, Ontario K1A 0S5

Telephone: (613) 996-8888

The Science Procurement Manager will be responsible for the management of the contract which may result from this invitation.

SCIENTIFIC AND TECHNICAL PROPOSAL:

Your proposal should include:

a) a description of the tasks you propose to undertake to fulfill the objectives of the Statement of Work.

b) a proposed task schedule including the number of man days per category of personnel required for each individual task.

c) organization and list of key personnel you propose to assign to the tasks, with a brief resume of their related qualifications and a description of their expertise in this particular area.

PRICING DATA REQUIREMENTS:

You shall provide the following pricing data:

1) price certification in accordance with DSS 1091 (9/73) terms and conditions, number 11.

2) price breakdown to include price for salaries and wages for each category of personnel, price for materials and supplies and overhead,

3) manpower price per task calculated in accordance with per diem rates for each category and with task schedule.

EVALUATION OF PROPOSALS:

Included in the proposal evaluation will be the following:

a) proposed strategy; (b) technical merit of proposal; (c) capability of personnel (knowledge and expertise); (d) organization and managerial competence; (e) commitment to delivery and schedule; (f) Canadian economic benefit; (g) commitment to work and to terms and conditions; (h) price.

ECONOMIC BENEFIT AND FOREIGN CONTENT:

Your proposal must indicate the extent of any non-Canadian content and price in Canadian dollars and also any economic benefit to Canada which may arise as a result of the work being contracted to your Company.

REPORTS:

The contractor will be required to submit brief monthly progress reports describing the work completed and relating to the task schedule. In addition, at such a time or times as the Scientific Authority may request, the contractor shall submit all copies of all data and other information obtained while performing the work under this contract.

A draft of the final report shall be submitted for review by

March 1, 1976. The contractor shall revise and submit a final report to the Scientific Authority not later than March 31, 1976. The final report is to be submitted in 100 copies and is to contain a description of analytical and sample handling procedures used, presentation of results of organic component classification for all samples, listing and chemical description of specific organic compounds identified for all samples, listing of semi-quantitative heavy metal analysis and measured concentrations of total vanadium for all samples, discussion of procedures used and modifications developed, recommendations concerning means of carrying organic analysis program forth into the receiving waters, conclusions relating to the chemical character of the organic component of wastewater samples and references cited.

One copy of all reports shall be submitted to the Science Procurement Manager.

TERMS AND CONDITIONS:

Provisions of General Conditions DSS 1053 (revised) shall apply to and form part of any resulting contract in lieu of the general conditions referred to on the reverse of page one.

The following have been invited to submit a proposal on this study:

University of Calgary

University of Alberta